Nitrous oxide emission dynamics and emission factors of two Finnish wastewater treatment plants

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Abstract of the master's thesis

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Abstract

Nitrous oxide (N_2O) emissions can contribute over 60% to the GHG emissions of a municipal wastewater treatment plant (WWTP). Thus, mitigation of N_2O emissions is important for carbon footprint reduction. This thesis studied the N_2O emissions of Kakolanmäki WWTP and Nenäinniemi WWTP located in Finland. Nitrous oxide concentrations were measured from the activated sludge processes with an off-gas hood. Measurement campaigns equal to 15 and 11 days were conducted at both plants. Nitrous oxide emission factors (EFs) were calculated for each measurement period, and the dynamics of the off-gas nitrous oxide concentrations were studied. The results were validated against long-term data from Viikinmäki WWTP.

The EFs for Kakolanmäki WWTP spring and summer measurement campaigns were 1.7% and 0.09% of total N-load, respectively. The EFs for Nenäinniemi WWTP were 1.3% and 1.0% of total N-load, respectively.

The off-gas N_2O concentration exhibited strong temporal variation also within the measurement campaigns. The hourly average off-gas N_2O concentrations during a measurement period varied from 6% to 432% of the average concentration. The lowest concentrations generally occurred 8–10 AM and the highest 8–11PM. Furthermore, the off-gasN_2O concentrations differed significantly between the compartments of an aeration line. Moderate positive correlation (Pearson's r=0.57) between the dissolved nitrite and off-gas nitrous oxide was found.

Water temperature differed significantly between the two measurement periods at both plants. At Nenäinniemi WWTP, full nitrogen removal was recognized as a potential N_2O mitigation measure during spring and winter season with colder water temperatures. At Kakolanmäki WWTP, several N_2O mitigation measures could be suggested: increasing COD to N ratio, DO concentration, SRT, and alkalinity.

To estimate the annual average EFs and to study the effects of N_2O mitigation measures, longer campaigns should be conducted with measurements conducted at several aeration compartments simultaneously. Or in the case of Kakolanmäki WWTP, which is located inside, plant exhaust gas line N_2O concentrations could be measured.

Keywords nitrous oxide, emission factor , greenhouse gas emissions , activated sludge , full-scale wastewater treatment plant

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Suorat typpioksiduulipäästöt (N_2O) voivat kattaa yli 60% kunnallisen jätevedenpuhdistamon kokonaispäästöistä, joten typpioksiduulipäästöjen mittaaminen ja päästöjä vähentävien toimien kartoittaminen on tärkeää jätevedenpuhdistamon hiilijalanjäljen pienentämiseksi.

Tässä työssä mitattiin Kakolanmäen ja Nenäinniemen jätevedenpuhdistamoiden typpioksiduulipäästöjä. Typpioksiduulikonsentraatioita mitattiin aktiivilieteprosessien ilmastusaltaista strippaantuvasta kaasusta. Molemmilla laitoksilla suoritettiin 15 päivän mittauskampanja keväällä ja 11 päivän mittauskampanja kesällä. Tulosten perusteella laitoksille laskettiin typpioksiduulipäästökertoimet. Lisäksi tutkittiin typpioksiduulikonsentraatioiden vaihtelua ajassa ja eri ilmastusaltaiden osissa. Mittauskampanjoiden tuloksia verrattiin yli vuoden laajuiseen dataan Viikinmäen jätevedenpuhdistamolta.

Kakolanmäen jätevedenpuhdistamon päästökertoimet kevään ja kesän mittausjaksoilta olivat 1.7% ja 0.09% sisääntulevasta typpikuormasta. Nenäinniemen jätevedenpuhdistamon päästökertoimet kevään ja kesän mittausjaksoilta olivat 1.3% ja 1.0%.

Typpioksiduulikonsentraatiossa havaittiin suurta ajallista vaihtelua myös mittauskampanjoiden aikana. N_2O konsentraatioiden tuntikeskiarvot vaihtelivat 6–432% mittauskampanjoiden keskiarvoista. Pienimmät konsentraatiot mitattiin yleensä kello 8–10 ja suurimmat kello 20–23. Lisäksi merkittäviä eroja havaittiin eri aerobisten lohkojen typpikonsentraatioissa. Positiivinen korrelaatio (Pearson korrelaatio= 0.57) havaittiin liuenneen nitriitin ja strippaantuvan typpioksiduulin välillä.

Molemmilla laitoksilla jäteveden lämpötila erosi selkeästi kevään ja kesän mittausjaksojen välillä. Nenäinniemen jätevedenpuhdistamolla jatkuva kokonaistypenpoisto voisi vähentää typpioksiduulipäästöjä kevät- ja talvikaudella. Kakolanmäellä COD:N –suhteen, DO konsentraation, lieteiän ja alkaliniteetin nostaminen voisivat vähentää N_2O päästöjä. Jatkotutkimuksia suositellaan, jotta päästöjenvähennyskeinojen tehokkuutta voidaan mitata.

Avainsanat typpioksiduuli, päästökerroin, kasvihuonekaasupäästöt, aktiiviliete, täyden mittakaavan jätevedenpuhdistamo

Preface

This thesis was completed as a part of ongoing research project on nitrous oxide emissions of Finnish wastewater treatment plants within the Water and Environmental Engineering department at Aalto University. The project has been funded by Aalto University, Finnish Water Utilities Association (FIWA), Turun seudun puhdistamo, Jyväskylän Seudun Puhdistamo, Nivos Ltd, Tampereen Vesi, and HS-Vesi.

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I would also like to thank Anna Kuokkanen and Kati Blomberg from HSY for providing me with the Viikinmäki WWTP data and sharing their expertise on nitrous oxide emissions.

Otaniemi, 17.8.2022

Helena Hilander

Contents

Symbols and abbreviations

AMO	Ammonia monooxygenase
AO	Anoxic, oxic activated sludge
AOA	Ammonia oxidizing archea
AOB	Ammonia oxidizing bacteria
AOR	Ammonia oxidation rate
A2O	Anaerobic, anoxic, oxic activated sludge
BOD	Biological oxygen demand
$CaCO_3$	Calcium carbonate
CAS	Conventional activated sludge process
COD	Chemical oxygen demand
Comammox	Complete ammonium oxidizing bacteria
CO_2	Carbon dioxide
CO_{2eq}	Carbon dioxide equivalent
Cu^{2+}	Copper ion
DO	Dissolved oxygen
EF	Emission factor
FB	Fixed bed biofilm reactor process
FTIR	Fourier transform infrared
GHG	Greenhouse gas
HAD	Heterotrophic aerobic denitrifying bacteria
He	Helium gas
HDN	Heterotrophic denitrifying bacteria
HAO	Hydroxylamine oxidoreductase
HNO_2	Nitric acid
H_2O	Water
IPCC	Intergovernmental Panel on Climate Change
IR	Infrared
LCA	Life cycle assessment
N	Nitrogen
Ne	Neon gas
NED	N-(1-naphtyl)-ethylenediamine
N_2	Nitrogen gas
NH_3	Ammonia
NH_4^+	Ammonium ion
NH_2OH	Hydroxylamine
NirK	Nitrite reductase
NO	Nitric oxide
NOB	Nitrite oxidizing bacteria
NOH	Nitrosyl radical
NoR, NorS	Nitric oxide reductase
NO_2^-	Nitrite
N_2O	Nitrous oxide
N_2O-N	Nitrous oxide nitrogen
NO_3^-	Nitrate
O_2	Oxygen
P	Phosphorous
PAX	Polyaluminium chloride
PE	People equivalent

ppmv	Parts per million volume
RAS	Return activated sludge
SA	Sulphanilamide
SBR	Sequencing batch reactor
SRT	Sludge retention time
SS	Suspended solids
WAS	Waste activated sludge
WWTP	Wastewater treatment plant

1 Introduction

Human-induced climate change is already changing ecosystem structure, shifting species, causing water and food scarcity, causing physical and mental health issues, and damaging infrastructure among other adverse impacts (IPCC, 2022). More damage is expected, and the severity and magnitude of the damage will depend on the number of degrees the climate is yet to warm (IPCC, 2022). Adjusting to the actualized and expected climate as well as mitigating the further warming of the climate are required in all sectors and geographical areas (IPCC, 2022).

In Finland, municipalities are actively contributing to the mitigation of climate change by setting carbon neutrality goals (SYKE, 2022). By the time of writing, 82 municipalities have committed to reduce their greenhouse gas emissions by 80 % by 2030 compared to the level in 2007. These ambitious goals motivate municipal wastewater treatment plants, among other municipal actors, towards sustainable operation.

Nitrous oxide (N_2O), commonly known as laughing gas, is a strong greenhouse gas that absorbs 265 times more energy compared to carbon dioxide making its global warming effect significant even in smaller quantities (IPCC, 2019). The direct nitrous oxide emissions produced in the nitrogen removal process of wastewater treatment can contribute over 60% to the total GHG emissions of a municipal wastewater treatment plant (Mölsä, 2020; Maite et al., 2022). Currently in Finland only one treatment plant, Viikinmäki WWTP in Helsinki, extensively tracks their N_2O emissions (HSY, 2019). Viikinmäki WWTP continuously monitors the off-gas N_2O emissions of the plant exit gas as well as the liquid phase N_2O concentrations of the aeration lines. Off-gas N_2O emissions have also been measured directly from the aeration lines (Kuokkanen et al., 2021; Myers, 2019; Kosonen et al., 2016). Short N_2O monitoring campaigns have also been conducted at four other Finnish WWTPs (Mikola et al., 2014). These campaigns include off-gas measurements during summer and winter conditions with less than a month of data collected in each plant.

N_2O emissions exhibit a complex multivariate dependency on wastewater treatment process variables, such as dissolved oxygen level, nutrient accumulation, alkalinity, pH, system shocks, and microbiological community (Vasilaki et al., 2019; Chen et al., 2020). Thus, the relative N_2O emissions vary between treatment plants, as well as inside a plant. Even plants with similar configuration, such as total nitrogen removal plants with anoxic-aerobic configuration, may have a difference of 2000% in their relative N_2O emissions proportional to the incoming nitrogen load (Gruber et al., 2021b). Due to the complex nature of N_2O emissions, accurate simulation models that could predict the N_2O emissions of a WWTP based on generally available process data are yet to be developed and measurement campaigns are currently the only means to accurately estimate the direct N_2O emissions of a WWTP (Vasilaki et al., 2019).

This thesis studies the nitrous oxide emissions of two Finnish municipal wastewater treatment plants, Kakolanmäki WWTP, Turku and Nenäinniemi WWTP, Jyväskylä. Two measurement campaigns equal to 15 days and 11 days were conducted at both plants. The first campaigns were conducted during March and April and the

second campaigns were conducted during May and June. At Nenäinniemi WWTP, measurements were conducted during both nitrifying and total nitrogen removal seasons. Nitrous oxide concentrations were measured from the gas stripping from the aerated compartments of the activated sludge processes. One to two measurement locations were measured per campaign. The measurement setup consisted of an off-gas hood and a Gasmet GT5000 Terra gas analyzer.

Based on the measured off-gas nitrous oxide concentrations combined with the aeration volumes of the activated sludge processes and the total nitrogen loads, nitrous oxide emission factors were calculated for each measurement period. Additionally, the spatial and temporal dynamics of the off-gas nitrous oxide concentrations, and the correlation between off-gas nitrous oxide and dissolved nitrite were studied. Furthermore, N_2O mitigation measures were suggested for Kakolanmäki WWTP and Nenäinniemi WWTP based on the comparison of the N_2O emission dynamics to the dynamics of process parameters. The results from Kakolanmäki WWTP and Nenäinniemi WWTP were compared to the N_2O emission data of Viikinmäki WWTP in Helsinki. Viikinmäki WWTP continuously measures their plant exhaust gas line N_2O concentrations, which provides a long-term data to validate the results of this thesis.

2 Background

2.1 Nitrous oxide production pathways

In wastewater treatment, nitrous oxide is mainly produced in biological nitrogen removal executed by nitrifying and denitrifying microorganisms (Maite et al., 2022). Nitrifying organisms convert ammonia (NH_3) to nitrate (NO_3^-) via nitrite (NO_2^-), while denitrifying organisms further convert (NO_2^-) and (NO_3^-) to nitrogen gas (N_2) (Kampschreur et al., 2009).

Microorganisms mainly responsible for nitrous oxide production are ammonia oxidizing bacteria (AOB) and heterotrophic denitrifying bacteria (HDN) (Chen et al., 2020). Other organisms that may produce N_2O include ammonia oxidizing archea (AOA), complete ammonium oxidizers (comammox), and nitrite oxidizing bacteria (NOB) (Maite et al., 2022). However, their contribution is considered less significant compared to AOB and HDN (Kits et al., 2019; Castellano-Hinojosa et al., 2018; Law et al., 2012). Ammonia oxidizing archaea yield 0.04–0.07% of N_2O per molecule of NO_2^-, while AOB yield 0.095–0.27% (Kits et al., 2019). Furthermore, AOA abundance has been observed to correlate negatively with N_2O emissions in four Spanish WWTPs (Castellano-Hinojosa et al., 2018). Comammox bacteria *Nitrospira inopinata* have been observed to produce similar quantities of N_2O to AOA in pure culture (Kits et al., 2019). NOB contribution to N_2O is widely accepted to be insignificant (Law et al., 2012).

The main N_2O production pathways can be classified into four categories: hydroxylamine oxidation, nitrifier denitrification, heterotrophic denitrification, and abiotic pathways (Maite et al., 2022; Chen et al., 2020). These pathways are further discussed in the following sections.

2.1.1 Hydroxylamine oxidation

Oxidation of accumulated hydroxylamine (NH_2OH) can cause increased N_2O production by enhancing NO_2^- or NO reduction to N_2O (Maite et al., 2022). Hydroxylamine is an intermediate of AOB nitrification, which refers to the conversion of ammonia (NH_3) to nitrite (NO_2^-) (Chen et al., 2020). In AOB nitrification, NH_3 is first oxidized to hydroxylamine (NH_2OH) by the enzyme ammonia monooxygenase (AMO), and NH_2OH is further oxidized to NO_2^- by the enzyme hydroxylamine oxidoreductase (HAO) (Maite et al., 2022). AOB nitrification is presented in Equation 1.

$$NH_3 \xrightarrow{AMO} NH_2OH \xrightarrow{HAO} NO_2^- \tag{1}$$

In the latest report series of International Water Association (IWA), Maite et al. (2022) note that the pathway to N_2O production in hydroxylamine oxidation remains under debate. First accepted pathway model that they present includes oxidation of NH_2OH to NO by HAO following with NO reduction to N_2O by a homologue of nitric oxide reductases (NoR). Second suggested pathway includes conversion of NH_2OH to nitrosyl radical (NOH) by HAO and chemical decomposition of NOH to N_2O. Caranto et al. (2017) proposed a third N_2O production pathway, in which NO

is an obligate intermediate of AOB nitrification alongside NH_2OH. This contradicts the predominant view on NH_2OH being the only intermediate (Maite et al., 2022). Figure 1 presents all the suggested pathways of N_2O production in NH_2OH oxidation.

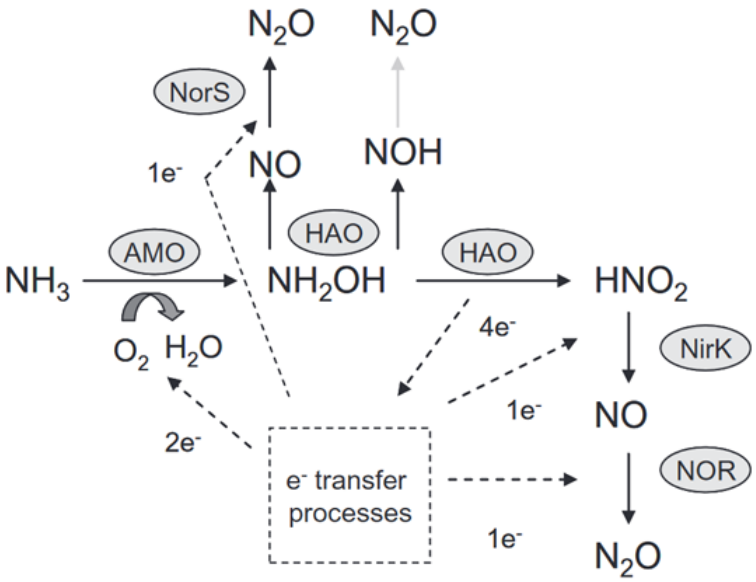


Figure 1: N_2O production pathways in hydroxylamine oxidation (Maite et al., 2022). Adapted from Ahn et al. (2010).

(HNO_2 = Nitric acid, NOH = Nitrolic acid, NorS = Nitric oxide reductase, NirK = Nitrite reductase)

2.1.2 Nitrifier denitrification

In nitrifier denitrification, AOBs use NO_2^- as an electron acceptor and convert it first to NO, which is further converted into N_2O (Equation 2) (Law et al., 2012). AOBs lack genes of N_2O reductase, thus making N_2O the final product of AOB denitrification (Chen et al., 2020). AOB denitrification occurs mainly in oxygen limited or anoxic conditions and during nitrite accumulation (Law et al., 2012; Chen et al., 2020).

$$NH_3 \xrightarrow{AMO} NH_2OH \xrightarrow{HAO} NO_2^- \xrightarrow{NirK} NO \xrightarrow{NoR} N_2O \tag{2}$$

2.1.3 Heterotrophic denitrification

Heterotrophic denitrification refers to the sequential reduction of NO_3^- to N_2 combined with oxidation of organic substrates (Kampschreur et al., 2009). NO_3^- is reduced to N_2 via NO_2^-, NO, and N_2O, thus making N_2O an obligate intermediate of denitrification (Equation 3). In complete denitrification, N_2O is fully reduced to nitrogen, but sub-optimal process conditions may cause incomplete reactions and N_2O accumulation (Law et al., 2012). Chen et al. (2020) list the presence of oxygen

and low COD levels as sub-optimal process conditions. They state that oxygen leads to incomplete denitrification because many denitrifying organisms prefer oxygen as electron acceptor over nitrogen compounds. Furthermore, they explain that low COD levels cause electron competition between denitrifying reductases, which may lead to incomplete N_2O reduction. The N_2O produced in the anoxic zones during denitrification is mainly emitted in the aerated zones due to aeration enhanced gas stripping (Law et al., 2012).

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2 \tag{3}$$

Heterotrophic denitrifying organisms (HDNs) include N_2 producing denitrifiers capable of complete denitrification, but also incomplete denitrifiers (Holmes et al., 2019). Some incomplete denitrifiers have N_2O as the final product because these organisms gain around 80 % of the energy of complete denitrification without converting N_2O forward (Law et al., 2012).

HDNs generally denitrify only in anoxic conditions because oxygen inhibits their production of denitrification reductase enzymes (Chen et al., 2020). However, heterotrophic bacteria that are capable of denitrification also in aerobic conditions have been found recently (Rajta et al., 2020). These bacteria are referred to as heterotrophic aerobic denitrifying bacteria (HAD).

2.1.4 Abiotic pathways

Abiotic pathways include different types of chemical reactions observed to produce N_2O in wastewater treatment (Chen et al., 2020). For example, hydroxylamine may react with oxygen (Equation 4) producing nitrous oxide (Chen et al., 2020). Hydroxylamine may also produce N_2O by reacting with nitrous acid (Equation 5) (Soler-Jofra et al., 2016). Furthermore, redox-active metals, such as iron and manganese, and organic substances, such as humic and fulvic acids, may react with nitrogen cycle intermediates producing N_2O (Zhu-Barker et al., 2015). Abiotic pathways typically produce minority of N_2O emissions but may be significant for example in advanced N-removal processes, such as SHARON (Soler-Jofra et al., 2016).

$$NH_2OH + 0.5O_2 \longrightarrow 0.5\mathrm{N_2O} + 1.5H_2O \tag{4}$$

$$NH_2OH + HNO_2 \longrightarrow \mathrm{N_2O} + 2H_2O \tag{5}$$

2.2 Factors affecting nitrous oxide emissions

Nitrous oxide emissions have a multivariate dependency on process parameters (Vasilaki et al., 2019). This section discusses single process parameters that impact the N_2O emissions. Due to the multivariate dependency, a change in a single process factor may not always lead to similar change in emissions.

Process parameters, whose impact on nitrous oxide emissions has been studied include dissolved oxygen level (DO), nitrite and ammonia accumulation, alkalinity, pH, temperature, COD to N ratio, and system shocks and rapid changes (Daelman et al., 2013; Gruber et al., 2021b; Kampschreur et al., 2009; Kosonen et al., 2016; Kosonen, 2013; Law et al., 2012; Myers, 2019; Vasilaki et al., 2019).

2.2.1 Dissolved oxygen

Sufficient dissolved oxygen (DO) level is required for optimal nitrification (Kampschreur et al., 2009). Low DO leads into increased nitrifier denitrification, which may increase N_2O emissions (Vasilaki et al., 2019; Kampschreur et al., 2009; Chen et al., 2020). According to a review paper by Law et al. (2012), maximum N_2O production rates have been observed with DO concentrations ranging from 0.1 to 0.3 mgO_2/L in the nitrifying compartments. A review paper by Chen et al. (2020) considers DO concentrations below 0.5 mgO_2/L as oxygen-limited conditions that can stimulate nitrifier denitrification.

On the contrary, DO is undesirable in the denitrifying compartments (Kampschreur et al., 2009). Many denitrifying organisms prefer oxygen as electron acceptor over nitrogen compounds, and thus, low oxygen levels are needed for efficient denitrification. Similar to nitrification, heterotrophic denitrification has been observed to produce the highest N_2O emissions at DO range of 0.1 to 0.3 mgO_2/L (Law et al., 2012).

2.2.2 Nitrite and ammonia accumulation

Nitrite accumulation has one of the strongest correlations with increased N_2O emissions (Gruber et al., 2021b; Vasilaki et al., 2019). Gruber et al. (2021b) found a significant correlation (r =0.65, p = 0.048) between effluent nitrite concentration and N_2O emissions in a study of 14 long-term measurement campaigns. Additionally, Vasilaki et al. (2019) noted a general trend of correlation between elevated N_2O emissions and nitrite concentration in a review article. The main N_2O production pathways associated with nitrite accumulation include nitrifier denitrification under low dissolved oxygen levels ($<$ 1 mgO_2/L), and heterotrophic denitrification in anoxic conditions (Chen et al., 2020).

Correlation between increased ammonia load and nitrous oxide emissions has also been observed (Kosonen et al., 2016; Myers, 2019). Kosonen et al. (2016) found a significant delayed correlation between NH_4^+ load of the aerated zones and N_2O emissions in hourly level (R= 0.74, p= 0.00, n=24). The finding is based on a one-year online monitoring campaign at Viikinmäki WWTP in Helsinki, Finland.

Similarly, Myers (2019) observed N_2O peaks shortly after ammonia load peaks in a two-week continuous online measurement campaign conducted at Viikinmäki WWTP.

2.2.3 Alkalinity and pH

Alkalinity refers to the concentration of titratable bases in water that neutralize acids (Dickson, 1981). Thus, alkalinity provides capacity for resisting acidification. Nitrification consumes alkalinity (Gerardi, 2016). Therefore, to maintain optimal nitrification, alkalinity need to be maintained. Kosonen (2013) observed significant negative correlations (r=0.61 and r=0.79) between N_2O emissions and alkalinity in two test periods of 10 days and 13 days at Viikinmäki WWTP. During the first test period, hydrated lime was fed into the process with an average rate of 78 g/s, and during the second test period, hydrated lime feeding rate was 59 g/s. Other process conditions were stable during the experiment, thus the changes in N_2O levels are assumed to be caused by the changes in alkalinity.

Negative correlation (r=0.65) between N_2O emissions and alkalinity was also observed by Kosonen (2013) in an eight-month-long continuous online measurement at Viikinmäki WWTP. Nitrous oxide production was highest at alkalinity levels below 0.9 $CaCO_3$ mmol/L and lowest at alkalinity levels above 1.4 $CaCO_3$ mmol/L. Low alkalinity was also observed to increase the diurnal variability of N_2O emissions. The pH of the process remained neutral during the observation period.

The pH affects N_2O production via its impact in the activity of nitrifying and denitrifying bacteria, activity of enzymes and the form of nitrogen in water (Chen et al., 2020). Both low pH levels below 6.5 (Pan et al., 2012) and high pH levels around 8 (Law et al., 2011) have been observed to accumulate nitrous oxide.

2.2.4 Temperature

Wastewater temperature affects N_2O production via altering reaction equilibria, enzyme activities, and gas solubilities (Zhang et al., 2017; Kampschreur et al., 2009). Disturbances in temperature cause imbalances between ammonia and nitrite oxidation reactions, causing nitrite accumulation that may lead to increased N_2O emissions (Zhang et al., 2017). Zhang et al. (2017) also found that temperature affects the activity of enzymes involved in nitrous oxide production. They found that optimal activity and lowest N_2O accumulation occurred at 25 degrees Celsius in lab-scale denitrifying biofilters. On the other hand, increased temperature decreases the solubility of N_2O, thus increasing the stripping of emissions (Kampschreur et al., 2009).

The correlation between temperature and N_2O emissions varies in full scale long-term monitoring campaigns due to the multivariate nature of N_2O emissions (Kosonen et al., 2016; Daelman et al., 2013). Daelman et al. (2013) observed a negative correlation between wastewater temperature and N_2O emissions with a time lag of 2–3 months in a long-term (more than a year) online monitoring campaign at Kralingseveer WWTP in the Netherlands with total nitrogen removal. The process consists of a plug flow reactor and two parallel carousel reactors. In contrast, Kosonen et al. (2016) found no significant correlation between daily average N_2O emissions

and water temperature in a year-long online monitoring campaign at Viikinmäki WWTP in Finland with total nitrogen removal and anoxic-aerobic activated sludge process. Generally, N_2O emissions might exhibit strong seasonal variation, but this not the case in all WWTPs (Vasilaki et al., 2019; Gruber et al., 2021a).

2.2.5 COD to N ratio

COD provides a carbon source for denitrification, and low COD to N ratio leads to incomplete denitrification and increased N_2O production (Maite et al., 2022). However, the optimal ratio between COD and N requires research (Chen et al., 2020). Law et al. (2012) state that generally COD to N ratio above 4 is required for complete denitrification, but different bacterial populations may have varying resilience to COD limitation. Furthermore, the type of carbon source affects the effectiveness of denitrification (Lee et al., 2019). Methanol as a carbon source has been observed to reduce N_2O more effectively compared to other carbon compounds, such as ethanol or acetate (Lee et al., 2019).

2.2.6 System shocks and rapid changes

Rapid changes in activated sludge process parameters, such as in influent load, ammonia concentration, and aeration, have been found to increase nitrous oxide emissions (Kosonen et al., 2016; Kampschreur et al., 2008b; Yu et al., 2010). Kosonen et al. (2016) observed increase in the average N_2O emissions during periods of high diurnal variation of influent load during a one-year online monitoring campaign at Viikinmäki WWTP, Finland. Kampschreur et al. (2008b) found that pulse NH_4^+ additions increase N_2O emissions in laboratory scale batch reactor with nitrifying culture under aerobic conditions. Furthermore, Yu et al. (2010) detected a peak in N_2O production during the transition from anoxic to aerobic conditions in laboratory scale nitrifying culture. The N_2O peak was found to have positive correlation with ammonia accumulation during the anoxic phase.

2.3 Nitrous oxide emission mitigation

Mitigation measures for N_2O emissions are important in reducing the total carbon footprint of wastewater treatment plant (Maite et al., 2022; Mölsä, 2020). Currently recognized mitigation strategies include optimal aeration intensity and dissolved oxygen level, preventing ammonia peaks, avoiding nitrite accumulation, providing sufficient carbon source to complete denitrification, maintaining neutral pH, and providing copper additive for denitrification (Vasilaki et al., 2019; Chen et al., 2020). Additionally, control of the microbial population as a N_2O mitigation strategy has raised interest in recent years (Chen et al., 2020). N_2O mitigation measures are generally in line with measures that maintain effective nutrient removal process (Vasilaki et al., 2019). Mitigation measures are summarized in Figure 2.

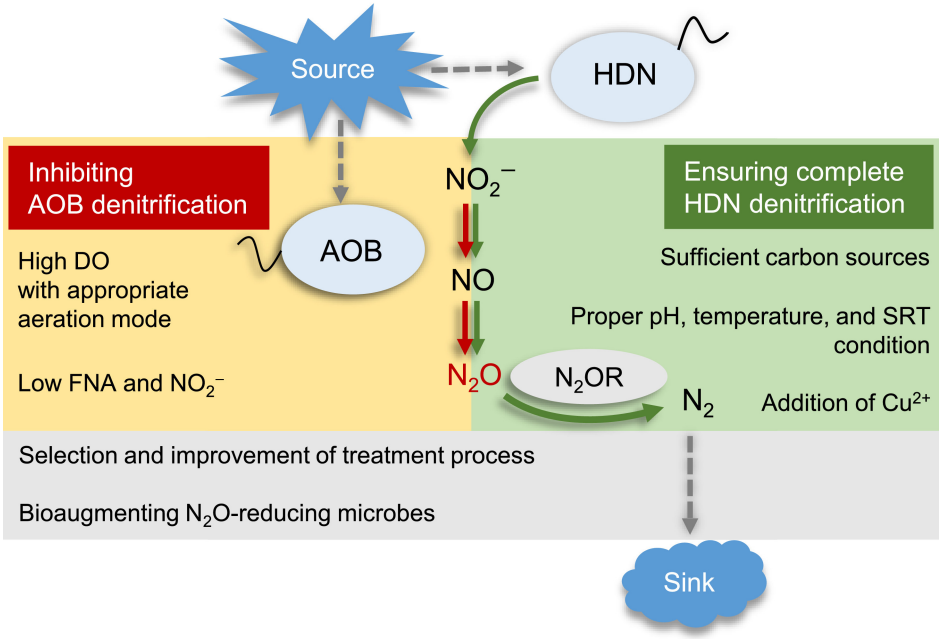


Figure 2: Mitigation strategies for nitrous oxide emissions in WWTPs (Chen et al., 2020.

Sufficient aeration prevents AOB denitrification and NH_2OH oxidization, thus reducing N_2O emissions (Chen et al., 2020; Vasilaki et al., 2019). Massara et al. (2018) found an optimal aeration level between 1.8 and 2.5 mgO_2/L with ASM2d-N_2O simulation model of a municipal anaerobic/anoxic/oxic (A2/O) WWTP with biological removal of organic matter, nitrogen and phosphorus. Higher aeration led to even lower N_2O emission but the additional decrease in emissions was estimated to be abolished by the increased aeration energy consumption. Furthermore, aeration intermittency has been studied as a means of reducing N_2O emissions, but the results remain unclear and likely depend on the nitrogen removal process type (Chen et al., 2020).

Alongside sufficient aeration, preventing the accumulation of nitrite reduces AOB denitrification, leading to lower N_2O emissions (Chen et al., 2020). The proper means

for preventing nitrite accumulation depend on the process type (Duan et al., 2021). For example, in fully aerated nitrifying processes a change to intermittent aeration may allow denitrification to occur during anoxic phases that will consume nitrate and nitrite (Béline et al., 2002). Another mean for avoiding nitrite accumulation is to equalize inflow, for example with equalization tanks (Vasilaki et al., 2019). Inflow equalization prevents sudden increases in COD that can lead to uncontrolled drop in dissolved oxygen levels, incomplete nitrification, and nitrite accumulation (Duan et al., 2021). Inflow equalization also reduces ammonia peaks that can increase N_2O emissions by increasing the ammonia oxidation rate (AOR), which may lead to nitrite accumulation and increased nitric oxide reduction to N_2O (Vasilaki et al., 2019). Third means to reduce nitrite accumulation is to increase the sludge retention time (SRT) (Kampschreur et al., 2008a). Longer SRT allows sufficient growth of NOB and ensures efficient nitrification.

Carbon source allows complete nitrogen removal and reduces N_2O emissions of denitrification (Chen et al., 2020; Vasilaki et al., 2019; Law et al., 2012). Carbon source may be provided as an additive or by allowing part of the influent water to bypass primary clarification. Methanol as a carbon source has been observed to reduce N_2O more effectively compared to other carbon compounds, such as ethanol or acetate (Lee et al., 2019).

Maintaining neutral pH (6.5–7) is recommended in order to provide optimal conditions for nitrifying and denitrifying bacteria, and preventing the inhibition of N_2O reducing enzymes (Chen et al., 2020; Vasilaki et al., 2019). Furthermore, copper additive has been observed to reduce N_2O and NO production (Chen et al., 2020). The N_2O reducing enzymes contain copper ions, and therefore lack of Cu^{2+} inhibits the reduction (Chen et al., 2020). However, if copper additives are to be tested in wastewater treatment plants, their effect on sludge handling should be considered (Maite et al., 2022).

Alongside considering the sources of N_2O to minimize emissions, utilization of N_2O sinks have started to raise interest (Chen et al., 2020). N_2O sinks include HDN, which have a N_2O reducing capacity up to 10 times larger than their N_2O production capacity (Conthe et al., 2019). Utilization of HDN requires control of the microbial community structure, for example by adding cultivated bacteria (Chen et al., 2020).

Knowledge gaps on the effectiveness of the nitrous oxide mitigation strategies exist due to lack of long-term monitoring campaigns (Chen et al., 2020). Future studies should especially focus on the trade-offs between GHG emissions, energy consumption and system performance (Vasilaki et al., 2019).

2.4 Nitrous oxide emission metrics

To compare N_2O emissions of WWTPs and track the success of mitigation measures, coherent emission metrics are required. Two metrics presented in *Guideline for the evaluation of nitrous oxide monitoring at WWTPs* by Gruber and Joss (2021a) are applied in this thesis: N_2O-N load for comparing absolute emissions and N_2O emission factor for comparing relative emissions to influent nitrogen load. These two metrics are defined in the following sections.

2.4.1 N_2O-N load

N_2O-N load presents the amount of nitrous oxide nitrogen emitted per hour (Equation 6). N_2O-N load gives the absolute amount of emissions and may be further applied to calculate the emission factor.

$$L_{N_2O-N} = C_{(N_2O-N,offgas)} Q_{Air} = \frac{N_2O_{measured}}{10^6} Q_{Air} \frac{p_N}{RT_N} M_N \tag{6}$$

L_{N_2O-N}	Emitted N_2O-N load	$[gN/h]$
$C_{(N_2O-N,offgas)}$	N_2O-N concentration in the off-gas	$[gN/Nm^3]$
Q_{Air}	Averaged air flow rate in the aeration basin, in standard cubic meters per hour	$[Nm^3/h]$
$N_2O_{measured}$	Measured N_2O concentration in the off-gas	[ppmv]
p_N	Standard pressure (101325 Pa)	[Pa]
T_N	Standard temperature (298 K)	[K]
R	Universal gas constant (8.314 J/mole/K)	[J/mole/K]
M_N	Molar mass of N_2O-N (28 gN/mole)	[gN/mole]

2.4.2 N_2O emission factor (EF)

In this thesis, the N_2O emission factor (EF) is defined as the percentage of the incoming nitrogen load emitted as nitrous oxide nitrogen (Gruber et al., 2021a). Equation 7 presents the formula for EF. Other definitions for EF also exist, which should be noted while comparing emission factors in the literature. EF may also be calculated for example as the share of removed total nitrogen emitted as nitrous oxide nitrogen.

$$E_{N_2O-N} = \frac{L_{N_2O-N,24h}}{L_N} 100\% \tag{7}$$

E_{N_2O-N}	N_2O emission factor	[%]
$L_{N_2O-N,24h}$	Daily average emitted N_2O-N load	$[gN/d]$
L_N	Daily average influent nitrogen load, including external co-substrates	$[gN/d]$

The daily average influent nitrogen load is calculated with Equation 8.

$$L_N = c_N \frac{V_{inflow}}{t_{sampling}} + L_{N,CoSubstrate} \tag{8}$$

c_N	inflow N concentration of flow proportional sample	$[gN/m^3]$
$\frac{V_{inflow}}{t_{sampling}}$	Daily average influent flow	$[m^3/d]$
$L_{N,CoSubstrate}$	Average N load fed to the process as an co-substrate	$[gN/d]$

($L_{N,CoSubstrate}$ refers to any additional nitrogen compounds added to the main process or digester alongside influent load)

2.5 The effect of temporal and spatial variation in N_2O emissions for representativeness of measurement results

Nitrous oxide emissions of wastewater treatment plants exhibit strong temporal and spatial variations (Vasilaki et al., 2019; Gruber et al., 2021a). Thus, measurement campaign results are affected by the length of the measurement campaign as well as the frequency and the locations of sampling.

A review of recent research by Vasilaki et al. (2019) shows that shorter campaigns typically result in smaller N_2O emission estimates. The review shows that nitrous oxide emissions exhibit strong temporal variation, which is not captured by short term campaigns. For short-term campaigns less than one month, the average emissions factor equals 0.8% (median 0.2 %). Medium-term campaigns between one month and one year average to an emission factor equal to 0.3 % (median 0.1 %) . Measurement campaigns are considered medium-term if they do not capture the total system temperature range. Long-term campaigns that consider seasonal trends and last at least one year average to an emission factor of 1.5% (median 1.7 %).

Short-term measuring campaigns may also capture exceptionally high N_2O emissions not representative of the average long-term behavior of a plant. Average emission factor as high as 8.5 % was measured by Myers (2019) in Viikinmäki WWTP in Finland during a two-week period in 2019 with continuous off-gas measurements from plant exit gas. This emission factor is 447 % of the average 12-month emission factor equal to 1.9 % measured in 2012–2013 by Kosonen (2016).

Furthermore, the sampling frequency affects measurement results, and diurnal and temporal variability may be missed with discontinuous measurement methods, such as grab samples (Gruber et al., 2020; Gruber et al., 2021a; Vasilaki et al., 2019). A review by Vasilaki et al. (2019) shows that discontinuous monitoring campaigns generally have smaller emission factors (average 0.44%, median 0.2 %) compared to continuous monitoring campaigns (average 1.2%, median 1.1%). All the campaigns studied were medium to long-term, lasting from one month to over a year. A finding by Gruber et al. (2020) further highlights the fast temporal dynamics of N_2O emissions: a seven-month long low N_2O emission period (EF <0.2%) was observed to change to high emissions (EF 4%) within four days at Lucerne WWTP, Switzerland. These high N_2O emissions at Lucerne lasted around a week. After a week, emissions decreased slightly but remained elevated for over a month compared to the low N_2O emission period that preceded the peak.

N_2O emission studies focusing on mechanisms of N_2O formation are suggested to have a temporal resolution of 1 point per 1 to 10 minutes according to the *Guideline for the evaluation of nitrous oxide monitoring at WWTPs* by Gruber and Joss (2021a). Studies measuring the emissions levels, four to eight measurements per hour is considered sufficient.

Alongside temporal heterogeneity, nitrous oxide emissions exhibit spatial variation (Gruber et al., 2021a; Mikola et al., 2014; Vasilaki et al., 2019; Gruber et al., 2020). Nitrous oxide emissions are produced in both aerobic and anoxic compartments of activated sludge process (Maite et al., 2022). However, aerated zones are typically the most significant source of nitrous oxide emissions, releasing around 80% of the emissions (Gruber et al., 2021b). Some of the nitrous oxide emissions measured from the aerated compartments may be produced in anoxic compartments, but due to low gas stripping in anoxic compartments, the gases remain dissolved until reaching the aerated compartments with larger air-liquid interface that allows larger gas stripping (Law et al., 2012).

Notable amount of nitrous oxide emissions may also arise from other process parts, such as secondary clarifier and reject water treatment (Vasilaki et al., 2019; Mikola et al., 2014). Mikola et al. (2014) observed that emissions from the secondary clarifier contributed between 5 and 33% of the total N_2O emissions in four Finnish WWTPs with denitrification-nitrification configurations. Measurements were conducted with an off-gas hood over several days in both summer and winter conditions. Furthermore, Kosse et al. (2017) measured higher dissolved N_2O concentrations in the secondary clarifier (average 10.99 ± 0.2 g/m^3) compared to the first nitrification zone of an aeration tank (average 9.87 ± 0.5 g/m^3). In other zones of the aeration line the N_2O concentrations were lower than the concentration of the first nitrification zone. The concentrations were calculated from grab samples with the NaBr salting out method at Ruhrverband WWTP in Bochum, Germany.

Regarding reject water treatment emissions, Vasilaki et al. (2019) reviewed emission factors of treatment processes of anaerobic digestion supernatant and found an average emissions factor of 2.1% of N-load. Treatment processes reviewed had several process types, including nitritation sequencing batch reactor, nitritation-ANAMMOX, nitritation SHARON, and Nitrification-denitrification sequencing batch reactor.

Difference in N_2O emissions may also appear between aeration lines, especially between lines with different feed sources (Gruber et al., 2020). Gruber et al. (2020) studied the impact of feed source in nitrous oxide emissions and observed that treatment of reject water in an aeration lane increased N_2O emissions by 80% while the nitrogen load increased only by 30%. Gruber et al. (2020) suggest monitoring all aeration lines with differing feed sources. For lines with common feed source, monitoring of one of them is considered sufficient.

Furthermore, N_2O emissions may differ between the compartments of a single aeration line (Gruber et al., 2020). Differences in aeration intensities between compartments may lead to different amounts of N_2O stripping (Law et al., 2012). Furthermore, N_2O emissions are produced through several pathways during nitrification and denitrification (Maite et al., 2022). Thus, N_2O production location depends on the location of the dominant production pathway.

2.6 Global research on N_2O emission factors

Long-term measurement campaigns are required to estimate plant specific N_2O emissions accurately (Vasilaki et al., 2019). N_2O emissions have a complex multivariate dependency on process parameters, which makes estimation of emissions without on-site measurements challenging (Maite et al., 2022). This section reviews results from long-term measurement campaigns studying the N_2O emissions of WWTPs. The reviewed campaigns are presented in Table 1.

Table 1: Nitrous oxide emission factors of wastewater treatment plants in long-term monitoring campaigns.

EF (% of N-load)	Measurement location	Sampling period	Sampling method	Treatment goal and (plant type)	Notes	Reference
1.9	Viikinmäki WWTP, Finland	12 months (2012-2013)	Continuous off-gas	Nitrogen removal AO	Nitrogen removal efficiency of biological treatment 60 %.	Kosonen et al., 2016
1.2	Viikinmäki WWTP, Finland	12 months (2018)	Continuous off-gas	Nitrogen removal AO		HSY, 2019
1.8	Altenrhein WWTP and Uster WWTP, Switzerland.	Minimum of one year	Continuous off-gas	Nitrification (CAS, FB, SBR)	Average of 3 processes. Nitrogen removal efficiencies of biological treatments 52,52, and 61 %.	Gruber et al., 2021b
0.9	Average of 10 plants	Minimum of one year	Continuous off-gas	Nitrogen removal		Gruber et al., 2021b
0.1	Moossee WWTP, Switzerland	More than a year	Continuous off-gas	Nitrogen removal (AO)	Nitrogen removal efficiency of biological treatment 67 %.	Gruber et al., 2021b
0.3	Schönau WWTP, Switzerland	More than a year	Continuous off-gas	Nitrogen removal (A2O)	Nitrogen removal efficiency of biological treatment 65 %.	Gruber et al., 2021b
0.1	Hofen WWTP, Switzerland	More than a year	Continuous off-gas	Nitrogen removal (AO)	Nitrogen removal efficiency of biological treatment 72 %.	Gruber et al., 2021b
1.6	Average of 14 plants.	Minimum of a year	Continuous off-gas	Nitrogen removal, nitrification, and carbon removal	EF range from 0.1% to 8%. (6% to 500% of mean value)	Gruber et al., 2021b
1.5	Average from review of several processes	Campaigns including seasonal trends	Continuous off-gas and grab samples		Median EF 1.7 %.	Vasilaki et al., 2019
1.2	Average from review of several processes	1 month to more than a year	Continuous off-gas		Median EF 1.1 %.	Vasilaki et al., 2019

(AO = anoxic, oxic activated sludge, A2O = anaerobic, anoxic, oxic activated sludge, CAS = conventional activated sludge process, FB = fixed bed biofilm reactor process, SBR = sequencing batch reactor)

Gruber et al. (2021b) report an average emission factor of 1.6 % based on 14 continuous measurement campaigns lasting over a year. In a review by Vasilaki et al. (2019), campaigns capturing seasonal variability (lasting from several months to over a year) average to an emission factor equal to 1.5 %. If only continuously monitored campaigns of the review are considered, the average emission factor equals 1.2 % (Vasilaki et al., 2019). However, large variance exists between individual measuring campaigns, which cannot be captured by average emission factors. In the study by Gruber et al. (Gruber et al., 2021b), emission factors of the 14 plants ranged between 0.1% and 8%, which corresponds to a range between 6% and 500% of the mean emission factor.

Plants with total nitrogen removal have on average a lower emission factor (average of 0.9 %) compared to plants with only nitrification as treatment goal (average of 1.8 %) (Gruber et al., 2021b). The averages are based on minimum one year long off-gas measurement campaigns conducted in three nitrification plants and in ten nitrogen removal plants. Variance exists also inside the category of total nitrogen removal plants: Three Swiss plants with total nitrogen removal and AO or A2O configurations (Moossee WWTP, Hofen WWTP, and Schönau WWTP) have been reported with emission factors of 0.1 %, 0.1 %, and 0.3 %, respectively (Gruber et al., 2021b), while Viikinmäki WWTP in Finland with total nitrogen removal and AO configuration reported an emission factor of 1.9% during 12-month monitoring campaign (Kosonen et al., 2016).

Wastewater treatment plants that have not conducted measurement campaigns may estimate emissions based on a general emission factor by IPCC (2019). However, a general emissions factor fails to capture the complex multivariate dependency of emissions and therefore cannot estimate plant specific emissions accurately. The current IPCC emission factor equals 1.6 % of total nitrogen load. Prior to 2019, the IPCC emission factor had a lower value. The current IPCC emission factor has been estimated based on 30 global datasets (IPCC, 2019). The maximum emission factor in the data is 4.5 % and minimum 0.016 %. The data includes measurement campaigns with varying lengths, such as ten 24-hour campaigns by Ahn et al. (2010) and six discontinuous monitoring campaigns with maximum four grab samples during five-month period by Foley et al. (2010). The dataset includes short-term measurement campaigns, which typically result in smaller emission estimates compared to long-term campaigns (Vasilaki et al., 2019; Gruber et al., 2021b). Therefore, the IPCC emission factor might underestimate the global average emission factor. On the other hand, despite being partly based on short-term data, the IPCC emission factor is equal to the average emission factor of 14 continuous long-term measurement campaigns estimated by Gruber et al. (2021b).

To conclude, long-term monitoring campaigns average close to the current IPCC emission factor of 1.6 % (Table 1). However, N_2O emissions have a large variance even between plants with same treatment goals and configurations, and even at the same plant during different seasons and years. For example, emission factor varies between 0.1% and 1.9% for total nitrogen removal plants with AO configuration. Thus, on-site measurement campaigns are required to track plant specific emissions accurately.

2.7 The uncertainty in the current N_2O emission estimates of WWTPs in Finland

Estimates of the nitrous oxide emissions of Finnish wastewater sector include a lot of uncertainty (Statistics Finland, 2019). Statistics Finland (2019) has estimated the total N_2O emissions of Finnish wastewater sector to equal 83 thousand tons of CO_2eq in 2017. Wastewater sector includes fish farming, industrial wastewater treatment, and domestic wastewater treatment. From the total GHG emissions of wastewater sector, N_2O emissions were estimated to account for 33 %. If only domestic wastewater treatment is considered, N_2O emissions are equal to 58 thousand tons of CO_2eq and the share of N_2O from the total GHG emissions of collected domestic wastewater treatment is estimated to be equal to 77 %.

Wastewater sector N_2O emissions are reported to have an uncertainty range between -94% and $+365\%$, which leads to an emission range between 5 thousand tons of CO_2eq and 386 thousand tons of CO_2eq (Statistics Finland, 2019). This large uncertainty of N_2O emission estimate arises from the application of a N_2O emission factor. Statistics Finland (2019) assumed single IPCC emission factor equal to 0.5 % of N-load for the entire wastewater sector, including fish farming, industrial wastewater treatment, and domestic wastewater treatment. This IPCC emission factor is reported to have an uncertainty range between -94% and $+363\%$, which leads to emission factor range from 0.03 % to 2.3 %. Global long-term N_2O measurement campaigns on WWTPs average to emissions factors 1.5–1.6 %, suggesting that 0.5 % is an underestimate of the average N_2O emissions at least for domestic wastewater treatment (Gruber et al., 2021b; Vasilaki et al., 2019). Thus, the N_2O emissions of Finnish domestic wastewater treatment, and consequently the N_2O emissions of Finnish wastewater sector, may be larger than the estimate.

A carbon footprint study by Awaitey (2020) demonstrates the strong dependence of N_2O emission estimates on selected N_2O emission factor. The carbon footprints of four Finnish's WWTPs were calculated during a three-year period. The average carbon footprint of the three-year period ranged between 45 and 82 $kgCO_2eqPE^-1Year^-1$. Direct nitrous oxide emissions from the wastewater treatment contributed on average 59 % of the total emissions during the three-year period. The carbon footprint calculation included chemical usage, energy consumption, treatment of wastewater, sludge treatment, and transport. The direct nitrous oxide emissions were estimated based on IPCC default emission factor equal to 1.6 % of N-load. Sensitivity analysis on N_2O emission factor was performed by decreasing the emission factor to 0.8 % and increasing the emission factor to 2.1 %. Sensitivity analysis showed that the carbon footprints of the four plants were impacted significantly by the changes in emission factor. The carbon footprint decreased around 25–30 % with the decrease in emission factor from 1.6 % to 0.8 %. The carbon footprint increased around 15–20% with the increase in emission factor from 1.6% to 2.1 %.

In order to reduce the uncertainty related to plant-specific as well as national N_2O emission estimates, online measurements of N_2O emissions are required at Finnish WWTPs. Viikinmäki WWTP in Helsinki is currently the only Finnish plant with continuous online monitoring of direct greenhouse gas emissions, including N_2O. Mölsä (2020) has estimated the carbon footprint of Viikinmäki WWTP in their thesis. The average carbon footprint of the wastewater treatment process in 2018 was 41 $kgCO_2eqPE^-1Year^-1$ with Excel-based Carbon Footprint Calculation Tool and 35 $kgCO_2eqPE^-1Year^-1$ with GaBi LCA tool. Direct nitrous oxide emissions from the wastewater treatment contributed on average 64 % of the total emissions according to Carbon Footprint Calculation Tool and 65 %

according to GaBi. The differences in results between these tools were mainly due to different constants applied in converting emissions to CO_2 equivalents. For example, Carbon Footprint Calculation Tool assumed stronger greenhouse gas impact for N_2O (factor of 298) compared to GaBi (factor of 265). During the study period of 2018, Viikinmäki WWTP total incoming nitrogen load was 4 874 940 kg/a, and the total nitrous oxide emissions were 93 645 kg/a (HSY, 2019). This leads to an average annual emission factor of 1.2 % of incoming nitrogen emitted as N_2O-N.

3 Research material and methods

3.1 Kakolanmäki WWTP, Turku

3.1.1 Overview

Kakolanmäki wastewater treatment plant is located in Turku, Finland and has been operating since December 2008 (Leino, 2022). The plant treats both municipal and industrial wastewater and has been dimensioned for 315 000 PE (PE calculated with $70 gBOD_{7ATU}/person/d$) (Leino, 2022). In 2021, the average daily inflow was equal to 83 534 m^3, but the daily inflow has been estimated to grow to 120 000 m^3 by 2030 (Leino, 2022). Part of the sewers connected to Kakolanmäki WWTP are combined sewers, and heavy rains and snow melting cause large inflow peaks. During periods of heavy rain or snow melting, daily inflow may triple and hourly inflow may increase five-fold (Turun seudun puhdistamo Oy, 2022b). The inflow temperature varies between 8 and 20 degrees Celsius depending on the season (Turun seudun puhdistamo Oy, 2022b). Kakolanmäki WWTP is located fully indoors and consists of a denitrification-nitrification activated sludge process with primary settling, tertiary sand filtration, and chemical phosphorus removal (Leino, 2022). In 2021, the plant fulfilled its environmental permit (ESAVI number 167/2014/2) by removing on average 86 % of the total nitrogen, 99 % of the total ammonium nitrogen, 98% of total phosphorus, 99 % of BOD_{7ATU}, and 97 % of COD_{Cr} (Leino, 2022).

The treatment process of Kakolanmäki is visualized in Figure 3 and described in detail at Turun seudun puhdistamo Oy website (2022b). As a first step of wastewater treatment, water flows through coarse screening, where the largest coarse impurities is separated. After coarse screening, ferrous sulphate is added to the water for chemical phosphorus removal. Second, water flows to a sand separation basin, in which sand and fat are separated, and water is pre-aerated. After sand separation, water is fine screened to remove smaller particulate impurities. From fine screening, water enters primary clarifiers, in which significant amount of the solid matter and some of the phosphorus settles. Alongside inflowing wastewater, waste activated sludge from aeration basins is pumped to the primary clarification. The settled sludge in the primary clarifiers is dewatered and transported for further treatment to Gasum Oy Topinoja Biogas Plant. The reject waters from sludge thickening and dewatering are pumped to the beginning of the process. From primary clarification, the water enters aeration basins including anoxic zones for denitrification and aerobic zones for nitrification. From the aeration basins, water and activated sludge is led into secondary clarifiers, in which the activated sludge and residual phosphorus settling is enhanced with polymer and ferrous sulphate. After secondary clarification, water is sand filtrated and led into the Baltic Sea. The plant has a separate two-line Actiflo®treatment unit for bypass water during inflow peaks. The treatment unit is for water that bypasses the aeration basins and uses ferrous sulfate, polymer, and microsand for treating water.

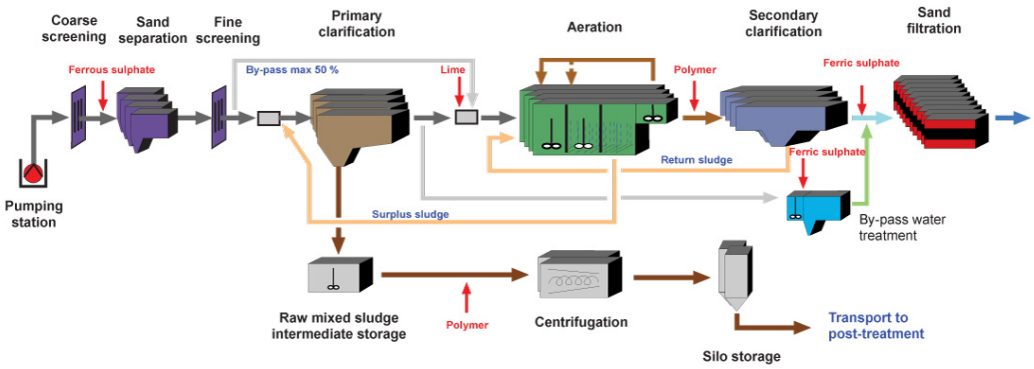


Figure 3: Kakolanmäki WWTP treatment process (Turun seudun puhdistamo Oy, 2022b).

3.1.2 Activated sludge process

Kakolanmäki activated sludge process is designed for total nitrogen removal with denitrification-nitrification configuration (Turun seudun puhdistamo Oy, 2022b). The activated sludge process occurs in four homogeneously fed lines divided into anoxic denitrifying zones and aerobic nitrifying zones (Turun seudun puhdistamo Oy, 2022a). To provide nitrate for the denitrification process, water from the end of the activated sludge process is circulated to the denitrifying zones at the beginning (Turun seudun puhdistamo Oy, 2022a). This circulation of water in an activated sludge process is referred to as nitrate recycle pumping or internal recycle, since it returns nitrate formed as the product of nitrification to the denitrifying zones, in which nitrate is further reduced to nitrogen gas. Alongside nitrate recycle pumping, sludge is recycled back into the aeration basins from secondary clarifiers (Turun seudun puhdistamo Oy, 2022a). The returned sludge is referred to as return activated sludge (RAS). Additionally, part of the sludge from the aeration basins is removed to maintain balanced microbial populations. This removed sludge is referred to as waste activated sludge (WAS). In Kakolanmäki WWTP, WAS is removed at the end of the aeration tanks (Turun seudun puhdistamo Oy, 2022a). The sludge age at Kakolanmäki WWTP is around 15 days during summer season, and 20 days during winter (Turun seudun puhdistamo Oy, 2022a). The influent wastewater partially passes by the primary clarifier, providing the denitrification process with carbon source (Turun seudun puhdistamo Oy, 2022a). Therefore, no external carbon source is usually needed. Aeration tanks are also fed with calcium carbonate to maintain alkalinity and pH that are consumed by nitrification (Turun seudun puhdistamo Oy, 2022a).

A single aeration basin consists of six compartments with sludge and seventh compartment, to which water flows as overflow (Turun seudun puhdistamo Oy, 2022a). Compartments 1 to 6 all have a depth of 15 meters, a volume of 2500 m^3, and a surface area of 167 m^2. Compartment 7 has a depth of 4 meters, volume of 350 m^3, and a surface area of 88 m^2. Compartments 1 and 2 are mixed and anoxic. Compartment 3 is alternatingly mixed (anoxic) and aerated (aerobic) depending on the ammonium level of compartment 5. Compartments 4 and 5 are aerated, and compartment 6 is aerated and mixed. The levels

of aeration in compartments 4,5, and 6 depend on the ammonium level of compartment 5. Compartment 7 is referred to as deoxidizing compartment. Water enters compartment 7 as overflow, and the compartment has mixing but no aeration. The aim is to remove excess air from water before recycling it back into the anoxic compartments at the beginning of the process.

The nitrate recycle pumping occurs from compartment 7 to compartment 1 (Turun seudun puhdistamo Oy, 2022a). The nitrate recycling is automated, and the recycled amount of water depends on the amount of inflow to aeration process. The target for the nitrate recycle pumping equals 300 % of the inflow, but the maximum capacity of nitrate recycle pumping, equal to 2000 m^3/h per line, typically limits the ratio to around 200 %. RAS is pumped from secondary clarifier to compartment 1 of an aeration line with two pipes (Turun seudun puhdistamo Oy, 2022a). RAS pumping is automated, and the recycled amount of sludge depends on the amount of inflow to aeration basins. The return ratio of RAS is around 125 % with a maximum of 1600 m^3/h per line. Waste activated sludge (WAS) is removed from compartment 6 of the aeration tank (Turun seudun puhdistamo Oy, 2022a). The WAS removal rate is on average 755 m^3/d and is automatically determined by target sludge age.

3.1.3 Chemicals added into the process

Kakolanmäki uses calcium carbonate for adjusting pH and alkalinity, polymer to enhance secondary settling, and ferrous sulfate for phosphorus removal (Turun seudun puhdistamo Oy, 2022a). Additionally, extra carbon source is added to aeration tanks if required (Turun seudun puhdistamo Oy, 2022a). According to the data received from the plant, calcium carbonate is fed into the wastewater before aeration tanks with an average rate of 3324 kg/d (2021 average), polymer is fed with an average value of 43 kg/d before secondary clarifier (2021 average), and ferrous sulfate is fed after coarse screening, with an average value of 6720 kg/d and to secondary clarifier with an average value of 2400 kg/d (Turun seudun puhdistamo Oy, 2022a). The fed amounts are controlled by mass flow meters.

3.1.4 Greenhouse gas emissions

The 2021 carbon footprint of Kakolanmäki WWTP has been estimated to be equal to 9 781 tons of CO_{2eq} (Leino, 2022). However, the environmental impact of the entire wastewater treatment process, including treatment plant, Gasum sludge processing and Turku District Energy (TSE) heat production, has been estimated to be negative and equal to -39 446 tons of CO_{2eq} (Leino, 2022).

The estimated amount of nitrous oxide emissions in 2021 was 7 471 tons of CO_{2eq}, which accounts for 76% of the 2021 carbon footprint estimate (Leino, 2022). The estimated amount of produced nitrous oxide in kilograms is equal to 28 200 kg (Leino, 2022). Thus, the estimate for the average daily nitrous oxide nitrogen load is equal to $\frac{28200kg\frac{28.02g/mol}{44.013g/mol}}{365d} = 49$ kg N_2O–N/d. The incoming total nitrogen load to Kakolanmäki WWTP in 2021 was equal to 4 200 kgN/d (Leino, 2022). Thus, the estimate for the 2021 annual average N_2O emission factor of Kakolanmäki is equal to 1.2% of the incoming nitrogen load.

The nitrous oxide emissions have been estimated based on data from Viikinmäki wastewater treatment plant located in Helsinki, Finland (Leino, 2022). Based on Viikinmäki data, a factor that relates nitrous oxide emissions to inflow volume has been calculated. This factor was equal to 0.00092464 kgN_2O/m^3 in 2021 (Sundell et al., 2022). Viikinmäki

WWTP monitors the nitrous oxide emissions with continuous online measurements from the exit gas of the plant, and several studies have been conducted from the measurements (e.g. Kosonen et al., 2016; Myers, 2019). Viikinmäki WWTP has of a similar activated sludge process to Kakolanmäki WWTP with denitrification-nitrification configuration (Kosonen, 2013; Myers, 2019). However, the nitrous oxide emissions are dynamic and correlate with process-specific factors such as nitrite accumulation, and influent load fluctuation (Vasilaki et al., 2019; Law et al., 2012). Therefore, estimating the nitrous oxide emissions of Kakolanmäki WWTP based on Viikinmäki WWTP data includes uncertainties.

3.2 Nenäinniemi WWTP, Jyväskylä

3.2.1 Overview

Nenäinniemi WWTP is located in Jyväskylä, Finland by Lake Päijänne. The plant treats both municipal and industrial wastewater and has an average PE of 228 000 (PE calculated with $70 gBOD_{7ATU}/person/d$) (Hynynen, 2022). In 2021, the average daily inflow was equal to 38 013 m^3 (Hynynen, 2022). During peak flows, daily inflow may double (Jyväskylän Seudun Puhdistamo Oy, 2022). The inflow temperature varies between 7 and 19 degrees Celsius depending on the season (Jyväskylän Seudun Puhdistamo Oy, 2022). Nenäinniemi WWTP process is placed partially indoors. The primary treatment and tertiary treatment are located inside plant buildings. Primary clarification, aeration basins and secondary clarifiers locate outdoors. Nenäinniemi WWTP consists of an activated sludge process with chemical phosphorus removal, primary settling, and tertiary disc filtration and UV-disinfection (Jyväskylän Seudun Puhdistamo Oy, 2022). The treatment goals for the activated sludge process are ammonia removal during winter and spring seasons (from November to July) and total nitrogen removal during summer and autumn seasons (from July to November) (Jyväskylän Seudun Puhdistamo Oy, 2022). Tertiary effluent is disinfected during open water season (Jyväskylän Seudun Puhdistamo Oy, 2022). In 2021, the plant passed its environmental permit, and removed on average 40 % of the total nitrogen, 99 % of the total ammonium nitrogen, 99% of total phosphorus, 99 % of BOD_{7ATU}, and 97 % of COD_{Cr} (Hynynen, 2022).

The treatment process of Nenäinniemi is visualized in Figure 4 and described in the annual treatment report of Nenäinniemi WWTP (Hynynen, 2022). First, inflow is pumped to the coarse screening. From coarse screening, water flows to aerated sand removal tank. From sand removal, the water flows to fine screening and into three primary clarifiers (total volume 5 700 m^3). In primary clarification, easily settleable solids, part of the phosphorus, and fat is removed from the water. From primary clarification, water is pumped to four aeration tanks (total volume 29 000 m^3). In the aeration tanks, dissolved organic and nitrogen compounds are removed from the water. From aeration, the water flows to four round secondary clarifiers (total volume 18 960 m^3), in which activated sludge is separated from the water. From the secondary clarifiers, return activated sludge is recycled back to the aeration, waste activated sludge is led to primary clarification, and water is led to tertiary treatment consisting of disc filtration and UV-disinfection. Disc filtration enhances suspended solids and phosphorus removal, and UV-disinfection improves the microbiological quality of water. Treated water is led to Lake Päijänne. Sludge settled at primary clarification is led to a sludge treatment process with anaerobic digestion that produces biogas, from which heat and electricity are generated for the plant. In 2021, the sludge treatment process produced 23 % of the plant electricity and nearly 100% of the

plant heating (Hynynen, 2022).

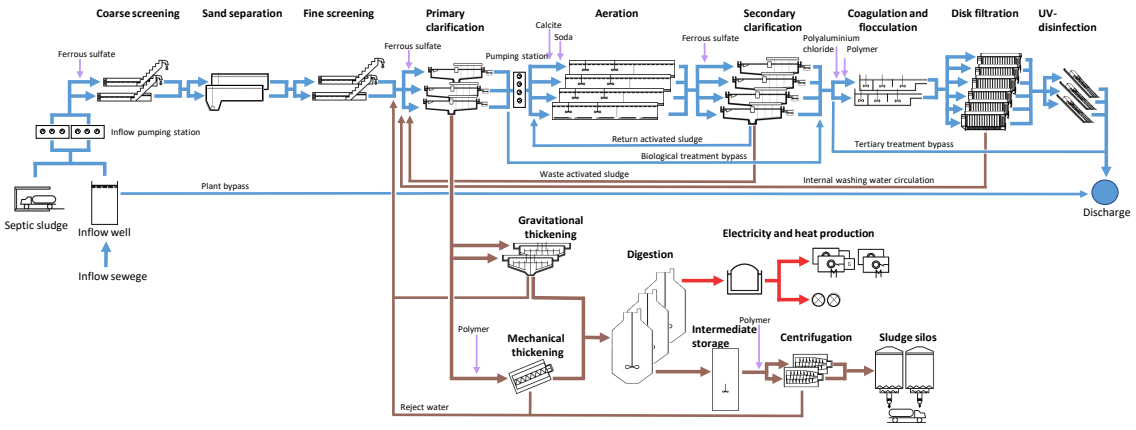


Figure 4: Nenäinniemi WWTP treatment process (Jyväskylän Seudun Puhdistamo Oy, 2022).

3.2.2 Activated sludge process

Nenäinniemi activated sludge process treatment goal is total nitrogen removal during summer season (July to November) and ammonia removal during winter season (Jyväskylän Seudun Puhdistamo Oy, 2022). Activated sludge process occurs in four lines divided into eight zones (Jyväskylän Seudun Puhdistamo Oy, 2022). The plant aims to feed the lines homogeneously. During winter, all eight zones are aerobic allowing nitrification. During summer, first two zones are anoxic allowing denitrification. RAS is recycled from secondary clarifiers to the beginning of aeration basins (Jyväskylän Seudun Puhdistamo Oy, 2022). RAS is mixed between the lines before returning it back. RAS recycling is automated, and the recycled amount of sludge depends on the amount of inflow water. The return ratio of RAS is typically 140–160%. WAS is removed from secondary clarifiers (Jyväskylän Seudun Puhdistamo Oy, 2022). The WAS removal rate depends on target sludge age, which varies between 10 and 22 days. The plant has no nitrate recycle pumping (Jyväskylän Seudun Puhdistamo Oy, 2022).

Previously, no additional carbon sources have been used in the process (Jyväskylän Seudun Puhdistamo Oy, 2022). However, starting from summer 2022 the plant is planning to provide a carbon source during denitrification period by allowing some water to pass primary clarification (Jyväskylän Seudun Puhdistamo Oy, 2022). To maintain neutral pH in the aeration, recycled calcite and soda ash are fed to water entering the aeration basins (Jyväskylän Seudun Puhdistamo Oy, 2022).

A single aeration basin consists of eight compartments (Jyväskylän Seudun Puhdistamo Oy, 2022). Compartments 1-2 and 7-8 have a depth of 4.7 meters, a volume of 750 m^3, and a surface area of 160 m^2. Compartments 3-6 have a depth of 6 meters, a volume

of 1063 m^3, and a surface area of 177 m^2. Compartments 1 and 2 are mixed (anoxic) during denitrification season. When only nitrification is used, compartments 1 and 2 are aerated (aerobic). Compartments 3-8 are aerated around the year. The aeration volumes are controlled by dissolved oxygen levels monitored from compartments 2,4,6, and 8. The start of the denitrification season is decided by the staff and compartments 1 and 2 are set from aerobic to anoxic manually.

3.2.3 Chemicals added into the process

Ferrous sulfate and polyaluminium chloride (PAX) are used for phosphorus removal (Jyväskylän Seudun Puhdistamo Oy, 2022). Ferrous sulfate is fed to the process prior to coarse screening and secondary clarification. PAX is fed to secondary clarification and tertiary treatment. The coagulant feeding is automated and depends on inflow rate and tertiary treatment phosphorus concentration. Additionally, polymer is fed to secondary clarification and tertiary treatment to enhance the settling of solids.

The pH and alkalinity are adjusted with recycled calcite and soda ash (Jyväskylän Seudun Puhdistamo Oy, 2022). These chemicals are fed to the pumping station of return activated sludge or to the lifting pumping station prior to the aeration lines. The pH and alkalinity adjustment chemicals are automatically fed according to the inflow rate.

3.2.4 Greenhouse gas emissions

Carbon footprint for Jyväskylän Seudun puhdistamo Oy, including Nenäinniemi WWTP and Korpilahti WWTP, has been estimated for 2020 (AFRY, 2022). The total carbon footprint estimate for 2020 was 14 153 tons of CO_{2eq}, from which Nenäinniemi WWTP accounted around 99%. Nitrous oxide emissions from Nenäinniemi WWTP were estimated to account for 40% of the total carbon footprint of Jyväskylän Seudun puhdistamo Oy. The amount of nitrous oxide emitted in 2020 was estimated to equal to 21 160 kg at Nenäinniemi WWTP. Nitrous oxide emissions were estimated based on IPCC emission factor equal to 1.6 % of total nitrogen load emitted as nitrous oxide nitrogen.

3.3 Measurement setup

This chapter presents the measurement setup used in the N_2O off-gas measurements at Kakolanmäki WWTP and Nenäinniemi WWTP. The direct N_2O emissions from the aeration basins were studied. The stripping N_2O was collected with a floating hood from the surface of an aeration tank. The hood was connected to a pipe that led gases to Gasmet GT5000 Terra gas analyzer. The gas analyzer measured continuously with 1 minute sampling time apart from measurement breaks. Figure 5 presents the measurement setup at Kakolanmäki WWTP aeration line during the spring measurement.

(a) Setup at Kakolanmäki WWTP. (b) Off-gas hood structure.

Figure 5: Measurement setup consisting of an off-gas hood and Gasmet GT5000 Terra gas analyzer.

3.3.1 Off-gas hood

The off-gas hood consisted of 1.17 m x 1.17 m plastic frame covered with tarp (Figure 5b). The plastic frame was connected to a stabilizing tube in the middle with metal wires. On top of the middle tube, a pipe led the stripping gas to a gas analyzer sensor. The hood was tied with ropes and metal wires to prevent movement in the aeration basins (Figure 5). Small adjustments were made to the hood alongside the measurement campaign to make it more robust. For example, styrofoam blocks were tied to each side of the hood for stabilization and preventing water accumulation on the hood.

3.3.2 Gasmet GT5000 Terra gas analyzer

Gasmet GT5000 Terra gas analyzer applies Fourier transform infrared (FTIR) spectroscopy to analyze gas compounds (Gasmet Technologies Oy, 2018). FTIR analyzers recognize molecules based on their unique infrared absorbance pattern. These absorption patterns depend on molecular structure. FTIR analyzer includes an infrared (IR) light source that emits IR light through sample gas. The sample absorbs some of the light, and the absorption spectrum is analyzed by an infrared detector. The detector records the signal in time domain and the signal is converted to frequency domain with Fourier transformation. Gasmet GT5000 Terra scans an infrared spectrum ten times per second. All spectra collected during measuring time (1 minute in this thesis) are co-added to reduce signal-to-noise ratio. The co-added spectrum is analyzed according to modified Classical Least Squares analysis algorithm. Gases that do not absorb infrared light cannot be recognized with Gasmet GT5000 Terra. These gases include diatomic elements, such as N_2 and O_2, and noble gases, such as He and Ne.

Sample pump flow equals 2 liters / minute, and the analyzer operates at ambient pressure and temperature. The operating temperature for Gasmet GT5000 Terra is from -5 to $40°C$ in short term-and from 5 to $30°C$ in long-term. Background measurement with nitrogen gas is recommended with 24-hour interval. The performance specifications of Gasmet GT5000 Terra are presented in Table 2

Table 2: Performance specifications of Gasmet GT5000 Terra gas analyzer.

Variable	Performance specification
Zero-point drift	<2% of measuring range per 24 h background measurement interval
Sensitivity drift	None
Linearity drift	<2% of measuring range
Temperature drift	<1 % of measuring range per 10 K temperature change. Ambient temperature changes are measured and compensated.
Pressure influence	1 % change of measuring value for 1 % sample pressure change. Ambient pressure changes are measured and compensated.
Background measurement	Recommended 24 h

3.3.3 Laboratory analyses

Alongside off-gas N_2O concentration, dissolved nitrite (NO_2^-) concentrations were measured to study the correlation between nitrite and N_2O. Nitrite concentrations were measured from grab samples that were taken from less than 50 cm depth in the aeration basins and less than 2 meters away from the off-gas hood.

Nitrite concentration was analyzed according to standard SFS 3029:E (1976). First, 5 ml of sample or its dilution was measured and filtered to a test tube with a 0.45 μm filter. Second, 125 μl of sulphanilamide (SA) solution was added to the test tube and the solution was mixed. After 4–6 minutes, 125 μl of N-(1-naphtyl)-ethylenediamine (NED) solution was added to the test tube and solution was again mixed. Next, the solution was kept in a

dark place for 20 -60 min, and the absorbance of the sample was measured at wavelength 545 nm with Shimadzu UV-1201 spectrophotometer. In spectrophotometer, an OG cell of 1 cm was used. A standard curve was applied to calculate the nitrite concentrations and the dilute factors were considered. Equation 9 presents the standard curve equation and Figure 6 presents a) the spectrophotometer and b) samples ready to be analyzed.

$$y = 294.1x - 0.794 \tag{9}$$

, where

x	Absorbance with range from 0 to 1.8	[-]
y	NO_2^- concentration	$[\mu g/l]$

(a) Shimadzu UV-1201 spectrophotometer (b) Water samples ready to be analyzed.

Figure 6: Nitrite concentration analysis.

3.4 Data processing

3.4.1 Unit conversion from ppmv to g/Nm^3

Gasmet GT5000 Terra gas analyzer reports gas concentrations in parts per million volume (ppmv), which refers to a certain volume of a gas diluted in one million volumes of air. To calculate nitrogen load (Equation 6) and emission factor (Equation 7), the nitrous oxide concentrations need to be converted to g/Nm^3 and further into gN/Nm^3.

One ppmv is equal to 1 micro liter of gas diluted in 1 liter of air. In order to convert the unit to g/Nm^3, the volume of the gas needs to be converted into mass. If ideal gas is assumed, following relation between mass m and volume V applies: $V_{gas} = \frac{V_m}{M_{gas}} m_{gas}$, where V_m refers to the molar volume of an ideal gas, and is equal to $22.4532 \frac{L}{mol}$ in normal

pressure $p = 1,01325$ bar and temperature $T = 298$ K. M_{gas} refers to molar mass and is equal to $44.01 \frac{g}{mol}$ for nitrous oxide. With this ideal gas relation, ppmv may be converted to g/m^3 as follows in Equation 10.

$$\begin{aligned}
\text{ppmv} =& 1 \frac{V_{gas}[\mu L]}{V_{air}[L]} \\
\text{ppmv} =& \frac{10^6 V_{gas}[L]}{V_{air}[L]} \\
\text{ppmv} =& 10^6 \frac{\frac{V_m[L/mol]}{M_{gas}[g/mol]} m_{gas}[g]}{10^3 V_{air}[m^3]} \\
\text{ppmv} =& 10^3 \frac{\frac{V_m[L/mol]}{M_{gas}[g/mol]} m_{gas}[g]}{V_{air}[m^3]} \\
\text{ppmv} =& 10^3 \frac{V_m[L/mol]}{M_{gas}[g/mol]} \frac{m_{gas}[g]}{V_{air}[m^3]} \\
10^{-3} \frac{M_{gas}[g/mol]}{V_m[L/mol]} \text{ ppmv} =& \frac{m_{gas}[g]}{V_{air}[m^3]} \\
\frac{m_{gas}[g]}{V_{air}[m^3]} =& 10^{-3} \frac{M_{gas}[g/mol]}{V_m[L/mol]} \text{ ppmv}
\end{aligned} \tag{10}$$

The nitrous oxide concentrations in unit g/Nm^3 were further converted into gN/Nm^3 by multiplying with the ratio of the molar mass of nitrogen gas N_2 and nitrous oxide N_2O ($\frac{28.02}{44.013}$).The concentrations in unit gN/Nm^3 describe the amount of nitrous oxide nitrogen per standardized cubic meter of air.

3.4.2 Unit conversion from m^3/h to Nm^3/h

In Nenäinniemi WWTP, the aeration volumes were measured as volumetric flows (m^3/h) from the aeration pipeline. These aeration volumes need to be converted to standard cubic meters (Nm^3) in order to estimate the N_2O–N load (Equation 6). By assuming ideal gas, conversion to standard cubic meters can be conducted with the ideal gas law based on the conservation of substance (Equation 11). The conversion equation does not consider the changes in relative moisture.

$$V2 = V1 \frac{P1}{P2} \frac{T2}{T1} \tag{11}$$

V1	Aeration flow in standard unit	$[Nm^3/h]$
V2	Aeration flow measured from the pipe	$[m^3/h]$
P1	Standard pressure: 101.32 kPa	$[kPa]$
P2	Pressure at the aeration flow measurement location	$[kPa]$
T1	Standard temperature: 273.15 K	$[K]$
T2	Air temperature at the measurement location	$[K]$

Two unknown variables, $V1$ and $T2$ were solved with Python scipy.optimize.minimize optimization function. The values of $V1$ and $T2$ were iterated until the error between Equation 11 and measured value of $V2$ was close to zero.

The value for the pressure at the aeration flow measurement location $P2$ is equal to $P1 + dP$, where dP stands for the pressure increase by compressors that pump the aeration air. The value of dP remains rather stable around year, and is approximately 54 kPa for

Nenäinniemi WWTP compartments 1,2,7, and 8. For compartments 3,4,5, and 6, dP is equal to 64.5 kPa.

3.4.3 Off-gas nitrous oxide concentration dynamics

The average, minimum, and maximum values for the off-gas nitrous oxide concentrations were calculated from the Gasmet measurement data without interpolation of missing values.

3.4.4 Correlation between off-gas nitrous oxide and dissolved nitrite

Correlation between off-gas nitrous oxide and dissolved nitrite was studied. Dissolved nitrite concentration was determined from a grab sample with the UV absorbance method. The nitrous oxide concentration was calculated as the average nitrous oxide concentration during the hour the nitrite sample was taken. The hourly average nitrous oxide concentration was calculated from the Gasmet measurement data without interpolation of missing values.

3.4.5 N_2O-N load and emission factor calculation

The aim of this thesis is to estimate the N_2O-N loads and emission factors for two wastewater treatment plants that consist of several aeration lines, each of which consists of several compartments. However, N_2O concentration measurements were conducted at maximum two compartments in each of the plants. This section discusses the data processing and assumptions made for estimating the total N_2O-N loads and emission factors based on limited data.

First, hourly average N_2O concentrations for all days of the week from Monday to Sunday were calculated for each measurement period. This day of the week representation for the N_2O concentrations was selected because it allows a similar representation for data recorded from different compartments during different time periods. Similar representation enables linear regression across compartment data, and thus the estimation of missing compartments. If an hourly average value was not available for some weekday, it was filled with the average value of the same hour from other weekdays. Missing hourly average from weekend was filled with the value of the same hour from the other weekend day. If some hourly average was missing from both weekend days, it was filled with the average value of the same hour from weekdays.

After the filling of the missing datapoints, the hourly average N_2O concentrations of unmeasured compartments were estimated. If N_2O concentrations had been measured from two compartments, the unmeasured compartments were estimated with linear regression (Figure 7). Linear regression was conducted for the hourly average N_2O concentrations for all days of the week separately. If N_2O concentrations were measured only from one compartment, all compartments were assumed to have the same N_2O concentrations equal to the measured values. The effects of these assumptions are reflected in the Discussions section.

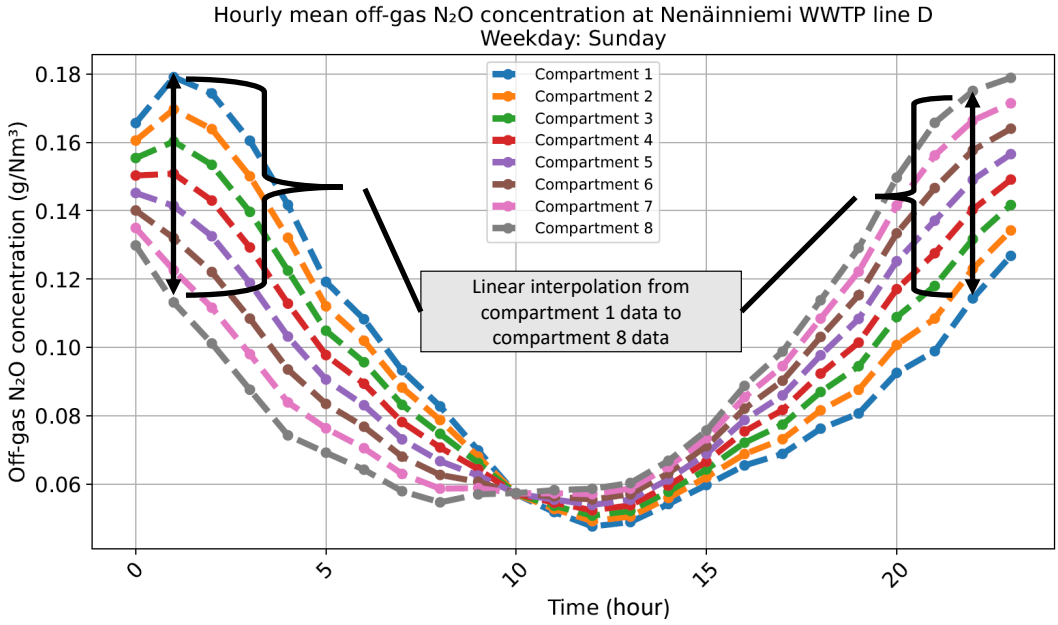


Figure 7: The N_2O concentrations of unmeasured compartments were estimated with linear regression if there was data available from two compartments. If data was available from one compartment, concentrations of all compartments were assumed equal.

After the N_2O concentrations of the unmeasured compartments had been estimated, the hourly N_2O-N loads for each compartment were calculated by multiplying the hourly average N_2O-N concentrations (gN/Nm^3) with the hourly aeration volumes (Nm^3/h). Unmeasured lines were assumed to have N_2O concentrations equal to the measured line, but the aeration volumes were collected from all lines. In Nenäinniemi WWTP, the aeration volume data was converted to standard units before N_2O-N load estimation according to Equation (11). The hourly total N_2O-N load of a plant was calculated as a sum of the hourly N_2O-N loads of all the compartments. The average and the median total N_2O-N loads of a plant were calculated by taking an average and a median from the hourly total N_2O-N load, respectively.

The EF of a WWTP during the measurement period was calculated by dividing the average N_2O-N load of the plant with the average total nitrogen load of the plant. The average total nitrogen load (gN/h) was calculated for the measurement periods by multiplying the hourly inflow data by the recorded or estimated total nitrogen concentrations and taking average of the products. Alongside the average EF, also median EF was calculated. The median calculation process was similar to the calculation of the average, apart from replacing all the average values with median values. Inflow data (m^3/h) was collected at hourly level and inflow total nitrogen concentration (gN/m^3) was measured once per week at Nenäinniemi WWTP and every other day at Kakolanmäki WWTP. Days that did not have total nitrogen concentration measured were filled with the average influent total nitrogen concentration from the measurement period. Data processing steps conducted in the calculation of the emission factor are presented in Table 3.

The nitrous oxide emissions are also presented as the share of nitrous oxide nitrogen from the removed total nitrogen. This metric is calculated by dividing the average N_2O-N

load of the plant with the average removed total nitrogen of the plant. The average removed total nitrogen (gN/h) was calculated for the measurement periods by multiplying the hourly inflow data by the recorded or estimated removed total nitrogen concentrations and taking average of the products. Days that did not have removed total nitrogen concentration measured were filled with the average removed total nitrogen concentration from the measurement period.

Table 3: Summary of the data processing steps conducted in the estimation of the N_2O-N loads and emission factors.

Data processing steps in calculating N_2O emission factor

1. Calculate hourly average N_2O concentrations for all days of the week.
2. Fill missing hourly averages by the following rules:
   (a) If the missing value is from Monday to Friday, fill the value with the average hourly N_2O concentration of weekdays that have data from that specific hour.
   (b) If the missing value is from weekend, fill the value with the hourly N_2O concentration of the other day of the weekend from that specific hour.
   (c) If the same hourly average is missing from both days of the weekend, fill the values with the average hourly N_2O concentration of weekdays that have data from that specific hour.
3. Estimate the hourly average N_2O concentrations of compartments that were not measured by the following rules:
   (a) If N_2O concentrations were measured from two compartments, estimate the unmeasured compartments with linear regression. Linear regression is conducted for the hourly average N_2O concentrations for all days of the week separately.
   (b) If N_2O concentrations were measured only from one compartment, assume all compartments to have the same N_2O concentrations equal to the measured values.
4. Calculate the hourly N_2O-N load for each compartment by multiplying the hourly average N_2O-N concentrations (gN/Nm^3) with the hourly aeration volumes of the compartment (Nm^3/h)
5. Sum all the hourly N_2O-N loads of all the compartments of the plant in order to estimate the hourly total N_2O-N loads of the plant
6. Estimate the average N_2O-N load of the plant from the measurement period by taking the average from the hourly total N_2O-N loads.
7. Estimate the emission factor (EF) of the WWTP during the measurement period by dividing the average N_2O-N load of the plant with the average total nitrogen load of the plant

3.5 Measurement campaigns

This section summarizes the measurement campaigns conducted in this thesis project. Four different measurement campaigns were conducted: 15-day spring and 11-day summer measurements at Kakolanmäki WWTP and 15-day spring and 11-day summer measurements at Nenäinniemi WWTP. The following sections describe in more detail each campaign, including the measurement locations, the amount of data recorded, measurement breaks, challenges with the measurement setup that may affect the result accuracy, nitrite sample-taking procedures, and the WWTP process conditions during the measurements. Table 4 presents general process parameters, such as inflows, nutrient concentrations, treatment results, and water temperatures from all of the measurement campaigns. The values presented in Table 4 have been received from the plant operators.

Table 4: Process parameters during the measurement campaigns at Kakolanmäki WWTP and Nenäinniemi WWTP. The values have been received from the plant operators.

	Kakolanmäki (21.3.-4.4.2022)	Nenäinniemi (11.4.-25.4.2022)	Kakolanmäki (30.5.-9.6.2022)	Nenäinniemi (13.6.-23.6.2022)
Inflow max (m3/d)	148281	81737	81253	37571
Inflow min (m3/d)	84448	49881	61405	34506
Inflow avg (m3/d)	115488	65148	68695	36071
Inflow max (m3/h)	8042	4330	5083	2873
Inflow min (m3/h)	2118	1036	1249	745
Inflow avg (m3/h)	4812	2775	2862	1563
COD, inflow (mg/l)	492	640	900	710
BOD, inflow (mg/l)	235	205	378	353
SS, inflow (mg/l)	227	424	370	503
P total, inflow (mg/l)	5.4	5.8	8.8	9.6
N total, inflow (mg/l)	39.3	43.5	59.0	72.5
COD, treated water (mg/l)	25.7	21.0	21.2	28.7
BOD, treated water (mg/l)	2.3	1.0	1.9	1.9
SS, treated water (mg/l)	1.8	2.6	<1	3.4
P total, treated water (mg/l)	0.1	0.1	0.1	0.1
N total, treated water (mg/l)	5.5	43.0	6.7	30.0
Treated COD (%)	95	97	98	96
Treated BOD7 (%)	99	100	99	99
Treated SS (%)	99	99	100	99
Treated P total (%)	98	98	99	99
Treated N total (%)	86	1	89	59
MLSS (g/l)	5.1	6.1	3.7	5.4
Alkalinity, inflow (mmol/l)	4.4	3.4	5.7	5.5
Alkalinity, outflow (mmol/l)	2.0	1.7	2.2	1.6
pH, influent	6.9	7.3	7.3	7.4
pH, effluent	6.9	7.2	7.0	7.0
Water temperature, aeration line (°C)	8.8	7.7 (after primary treatment)	14.2	14.5 (after primary treatment)
Dissolved oxygen (mg/l)	Compartment 6: 1.7	Compartment 2: 2.1 Compartment 8: 5.8	Compartment 4: 1.8 Compartment 6: 1.4	Compartment 4: 2 Compartment 8: 2.5

3.5.1 Kakolanmäki WWTP spring, 22.3.–4.4.2022

First measurement campaign was conducted at Kakolanmäki WWTP, Turku between 21.3.2022 and 4.4.20222. Kakolanmäki has four aeration lines that are fed with a common influent source. According to the plant staff, no significant differences in the treatment results of the four aeration lines had been observed prior to the measurement period. Thus, the off-gas measurements were conducted at line 2, which is located at the centre of the process and is expected to represent an average behaviour of the aeration lines. The hood was placed in the sixth compartment of aeration line 2 (Figure 8). From the 15-day measurement period, 203 hours (8.5 days) of data was recorded from compartment 6, including one weekend and 6 nights. Breaks in the recording occurred due to calibration of the device, adjustments of the hood, and unintentional shutdowns of the gas analyzer computer software during nighttime.

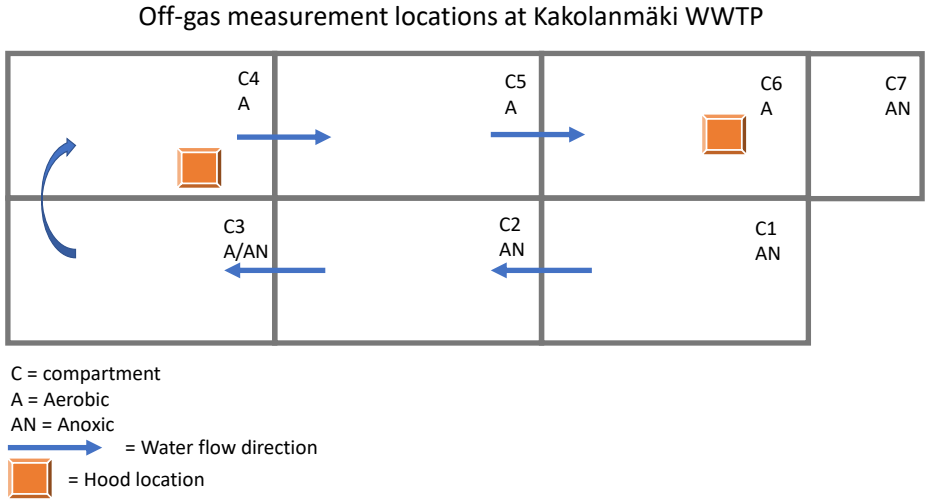


Figure 8: N_2O off-gas measurement locations at Kakolanmäki WWTP.

Gasmet analyzer calibration was conducted mainly with less than 25-hour intervals. The recommended calibration interval is 24 hours. Between Wed 30.3.2022 9AM and Fri 1.4.2022 2PM the measurement was run uninterrupted for 47 hours. The measurement was run uninterrupted also between Sat 2.4.2022 9AM and Mon 4.4.2022 10AM for 43 hours.

Additionally, 20 hours of data was recorded from compartment 4 between 27.3.2022 and 28.3.2022 (Figure 8). However, the pipe of the hood broke during the night due to very strong flow current and aeration. Due to tearing of the pipe, ambient air was mixed with the off-gas, making the data unusable.

Dissolved nitrite samples were collected 23.–25.3.2022 and 28.3.–3.4.2022 from compartment 6. In total, 24 nitrite samples were collected. The samples were taken 2-3 times per day, during morning, midday and afternoon. The precise time of the sample taking varied. The minimum nitrite concentration measured was 0.02 mg/l. The maximum measured nitrite concentration was 1.1 mg/l. The average measured nitrite concentration was 0.5 mg/l.

Table 4 presents general process parameters of Kakolanmäki WWTP from the measurement period. The average daily inflow during the measurement period was equal to 115 488 m^3/d, which accounts for 138% the daily average daily inflow in 2021 equal to 83 534 m^3/d (Leino, 2022). The average inflow nutrient concentrations for COD, BOD, SS, total P, and total N were slightly smaller than the average values of 2021. The most significant difference to 2021 average was 25% for total phosphorus. Other inflow nutrient concentrations were 10% to 24% smaller than 2021 averages (Leino, 2022). The removal-% during the measurement period differ less than 2.5% from the 2021 averages (Leino, 2022).

The water temperature during the measurement period was 8.8 °C, which is at the low end of the typical temperature range of Kakolanmäki WWTP. the typical range is from 8 °C to 20 °C. The pH of both the influent and the effluent was 6.9, and the average dissolved oxygen level at compartment 6 line 2 during the measuring period was 1.7 mg/l, which is 19% smaller than the 2021 average equal to 2.1 mg/l.

3.5.2 Nenäinniemi WWTP spring, 11.4.–25.4.2022

Spring measurement campaign at Nenäinniemi WWTP was conducted between 11.4.2022 and 25.4.2022. The plant has four aeration lines (lines A–D) with common influent water source and return sludge. The measurements were conducted at line D. The hood was placed in compartment 8 between 11.4 and 19.4, and in compartment 1 between 20.4 and 25.4 (Figure 9).

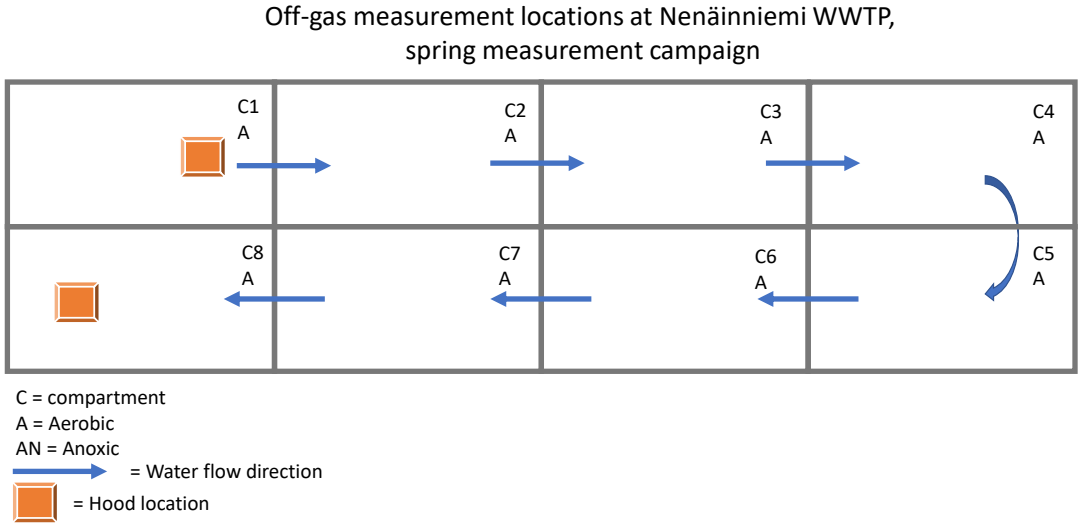
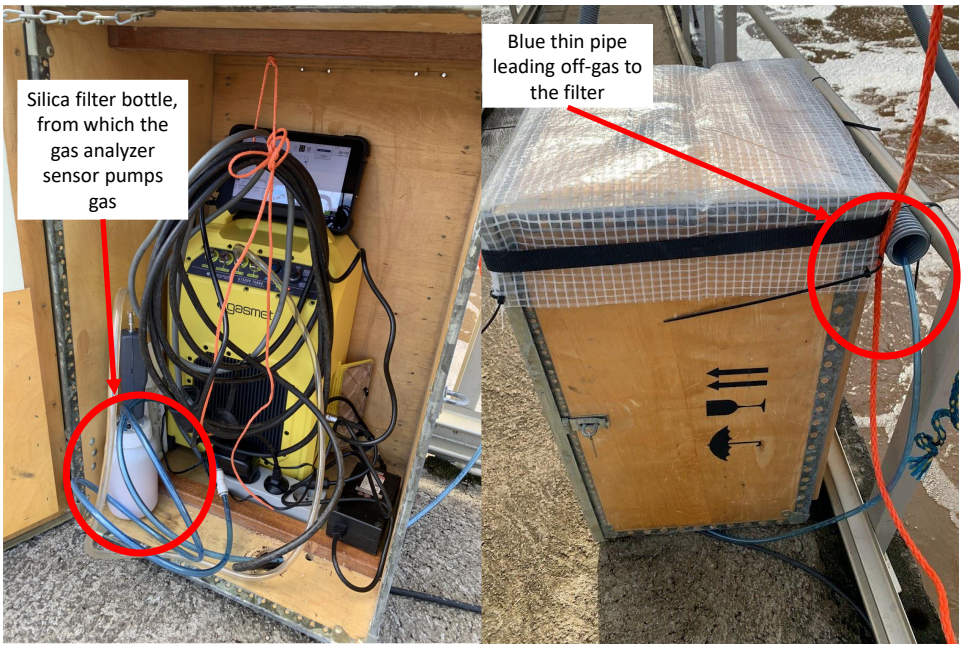


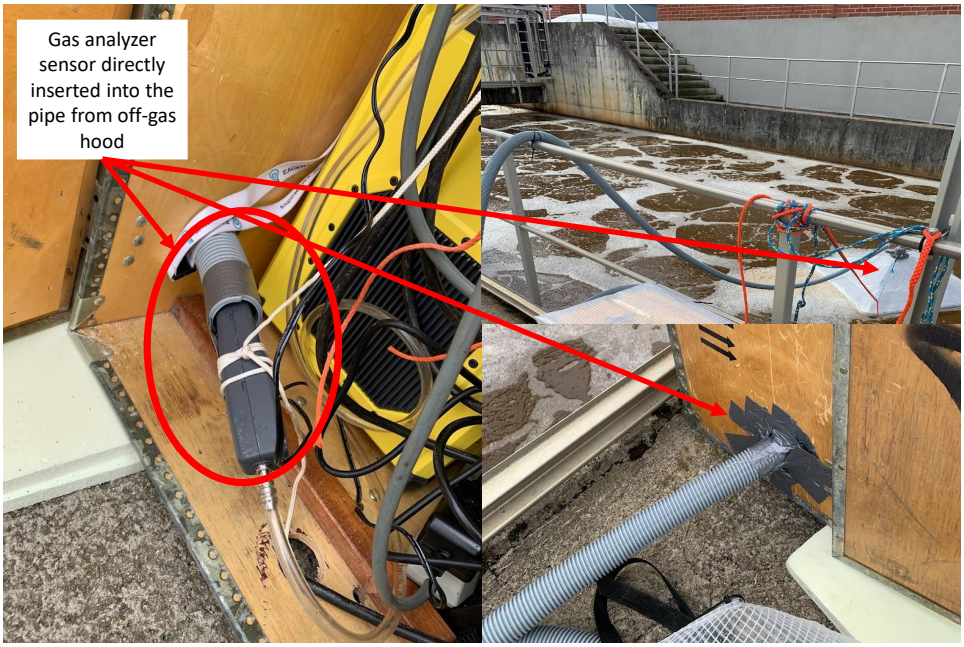
Figure 9: N_2O off-gas measurement locations at Nenäinniemi WWTP spring measurement campaign.

From the 15-day measurement period, 78 hours (3.3 days) of data was recorded from compartment 1, including one weekend and 4 nights. From compartment 8, 173 hours (7.2 days) of data was recorded, including one weekend and 7 nights. Breaks in the recording were due to calibration of the device, adjustments of the hood, and unintentional shutdowns of the gas analyzer computer software during nighttime.

Between 11.4 and 14.4, a silica filter bottle was used in the hose connecting the hood and the measurement device to prevent moisture from entering the gas analyzer (Figure 10a). The off-gas air was led to a silica filter bottle with a narrow pipe. However, on 13.4., the off-gases were measured directly from the off-gas pipe, and it was observed that the N_2O concentrations were higher without the filter (Figure 11). Therefore, from 14.4. onwards measurements were taken directly from the off-gas pipe and the silica filter was not used (Figure 10b). Data with the silica filter between 11.4 and 14.4 was included into the analysis with a correction factor of 2. The subsequent data points without filter and with filter were observed to have differences with magnitudes of 1.4, 1.6, and 2. The largest difference, 2, was used as a conservative correction factor.



(a) with silica filter



(b) without filter

Figure 10: N_2O off-gas measurement setup.

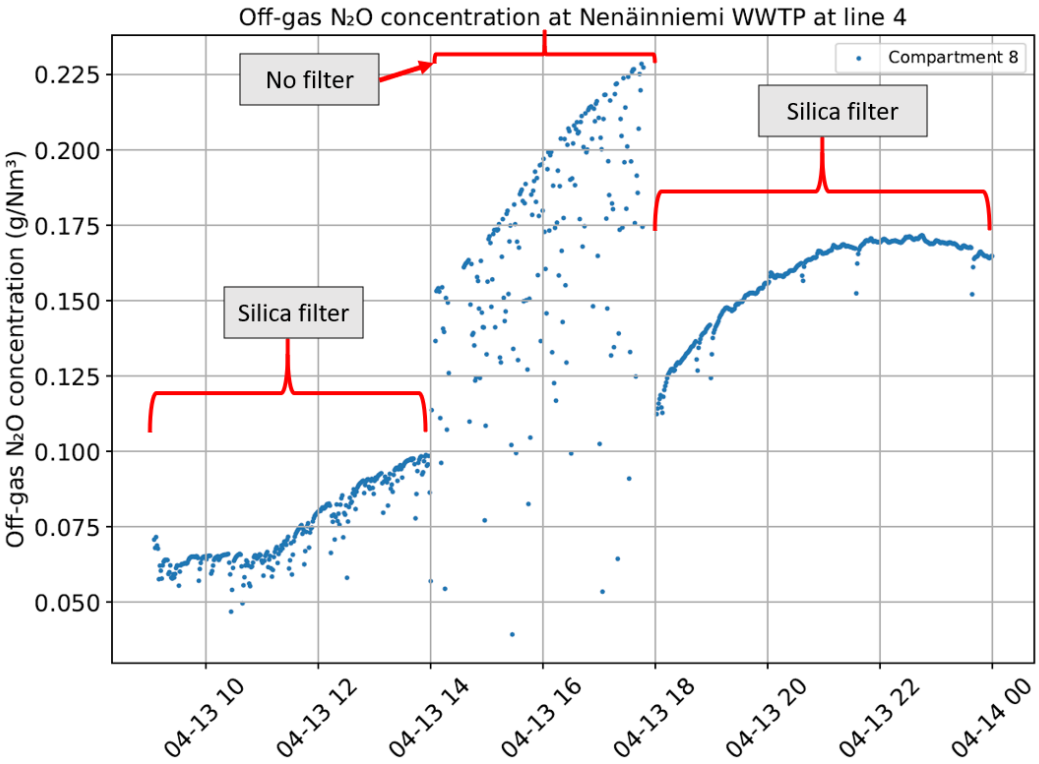


Figure 11: The effect of silica filter on N_2O off-gas measurements. Filter setup is presented in Figure 10a.

Dissolved nitrite samples were collected 12–23.4.2022 from compartments 1 and 8. In total, 7 samples were taken from compartment 1, and 14 samples were taken from compartment 8. The samples were taken 2 times per day, during morning and afternoon. The precise time of the sample taking varied. The minimum, maximum, and average nitrite concentrations at compartment 1 were 0.8 mg/l, 1.1 mg/l, and 0.9 mg/l, respectively. The minimum, maximum, and average nitrite concentrations at compartment 8 were 0.008 mg/l, 0.06 mg/l, and 0.02 mg/l, respectively.

At compartment 1, both flow current and aeration were high, which caused some airspace to the corners of the hood as they were lifted slightly. This might have diluted the N_2O concentrations if ambient air entered under the hood. However, the airspace was rather small and surfaced the water. Therefore, the possible dilution is expected to be insignificant.

Table 4 presents general process parameters of Nenäinniemi WWTP from the measurement period. The spring measurement campaign at Nenäinniemi occurred during snow melting period, and the inflows were higher than average. Influent flows up to 81 737 m^3/d were measured, which is 215% of the average inflow of 2021 equal to 38 013 m^3/d (Hynynen, 2022). The average inflow during the measurement period was 65 148 m^3/d, which is accounts for 171% of the average inflow of 2021. During the measurement period, the average inflow nutrient concentrations for COD, BOD, SS, total P and total N were 42%, 51%, 38%, 47%, and 47% smaller than the 2021 averages, respectively (Hynynen, 2022). The average removal-% for COD, BOD, SS, and total P differed less than 1% from 2021 averages (Hynynen, 2022). The removal-% for total nitrogen was only 1%, because

the activated sludge process was run fully aerobic with ammonia removal as the treatment goal. The ammonia removal rate during the measurement period was close to 100%.

The wastewater temperature was 7.7 °C, which is at the low end of the typical temperature range from 7 °C to 19 °C. The pH of both the influent and effluent was neutral. The average dissolved oxygen concentration at compartment 2 line D during the measurement period was 2.1 mg/l. No dissolved oxygen measurement was available at compartment 1. The average dissolved oxygen concentration at compartment 8 line D was 5.8 mg/l. National Easter holiday occurred between 15.4. and 18.4. Thus, Friday 15.4. and Monday 18.4. data from compartment 8 may not represent average consumption patterns of weekdays.

3.5.3 Kakolanmäki WWTP summer, 30.5.–9.6.2022

The second measurement campaign at Kakolanmäki WWTP, Turku was conducted between 30.5.2022 and 9.6.20222. The hood was placed in the fourth compartment of aeration line 2 from 30.5. to 6.6. and then moved to the sixth compartment of line 2 until 9.6.. Figure 8 presents the hood locations and the aerated compartments.

From the 11-day measurement period, 110 hours (4.6 days) of data was recorded from compartment 4, including 11 hours of data from the weekend and 5 nights. From compartment 6, 47 hours of data was recorded including 1 full night. Breaks in the recording occurred due to calibration of the device, adjustments of the hood, and unintentional shutdowns of the gas analyzer computer software during nighttime. No problems with the hood occurred.

Dissolved nitrite samples were collected 30.5.–8.6.2022 from compartments 4 and 6. In total, 5 samples were taken from compartment 4, and 5 samples were taken from compartment 6. One sample was taken per day, either during morning or afternoon. The minimum, maximum, and average nitrite concentrations at compartment 4 were 0.13 mg/l, 0.28 mg/l, and 0.16 mg/l, respectively. The minimum, maximum, and average nitrite concentrations at compartment 6 were 0.01 mg/l, 0.2 mg/l, and 0.08 mg/l, respectively.

Table 4 presents process parameters of Kakolanmäki WWTP from the measurement period. The average daily inflow during the measurement period was equal to 68 695 m^3/d, which accounts for 82% the daily average daily inflow in 2021 (Leino, 2022). The average inflow nutrient concentrations for COD, BOD, SS, total P and total N were 43%, 45%, 23%, 22%, and 18% larger than the 2021 averages, respectively (Leino, 2022). The average removal-% for COD, BOD, SS, total P, and total N differed less than 3% from the 2021 averages.

The average wastewater temperature during the measurement period was 14.2 °C, which is in the middle of the typical range. The pH of both the influent and the effluent was neutral. The average dissolved oxygen level at compartment 4 line 2 during the summer measurement period was 1.8 mg/l and 1.4 mg/l at compartment 6 line 2.

If the two measurement periods in Kakolanmäki WWTP during spring (22.3.–4.4.2022) and during summer (30.5.-9.6.2022) are compared, the average daily inflow was 41% smaller during summer measurements. The average influent nutrient concentrations for COD, BOD, SS, total P and total N were 83%, 61%, 63%, 62%, and 50% higher during the summer measurements compared to the spring measurements, respectively. However, the average influent nutrient loads (kg/d) differed less than 11% between the two periods. The removal-% differed at maximum 3%. The alkalinity of the inflow was 28% higher and the water temperature was 61% higher during the summer measurements compared to the spring measurements.

3.5.4 Nenäinniemi WWTP summer, 13.6.–23.6.2022

The second measurement campaign at Nenäinniemi WWTP, Jyväskylä was conducted between 13.6.2022 and 23.6.20222. During this measurement campaign, the process was run with denitrification-nitrification configuration, and the first two compartments of each aeration line were anoxic. The hood was placed in the 8th compartment of aeration line D from 13.6. to 20.6. and then moved to the 4th compartment of line D until 23.6.. The fourth compartment was selected instead of the the third compartment for practical reasons. It would have been challenging to gain access to electricity and charge the measurement device near compartment 3. Figure 12 presents the hood locations and the aerated compartments.

From the 11-day measurement period, 140 hours (5.8 days) of data was recorded from compartment 8, including one Saturday, half of Sunday, and 6 nights. From compartment 4, 67 hours (2.8 days) of data was recorded including 3 full nights. Breaks in the recording occurred due to calibration of the device, adjustments of the hood, and unintentional shutdowns of the gas analyzer computer software during nighttime. No problems with the hood occurred. No nitrite samples were collected from Nenäinniemi WWTP during summer measurement campaign due to time limitations.

Table 4 presents process parameters of Nenäinniemi WWTP from the measurement period. The average daily inflow during the measurement period was equal to 36 071 m^3/d, which accounts for 95% the daily average inflow in 2021 (Hynynen, 2022). During the measurement period, the average inflow nutrient concentrations for COD, BOD, SS, total P and total N were 35%, 16%, 26%, 13%, and 12% smaller than their respective averages for 2021 (Hynynen, 2022). The average treatment results for COD, BOD, SS, and total P differed less than 1.1% from 2021 averages (Hynynen, 2022). The removal-% for total nitrogen was 59%, which is 47% higher than the 2021 average. The average dissolved oxygen level at compartment 4 line D during the summer measurement period was 2.0 mg/l and 2.5 mg/l at compartment 8 line D.

If the two measurement periods in Nenäinniemi WWTP during spring (11.4.–25.4.2022) and summer (13.6.–23.6.2022) are compared, the average daily inflow was 45% smaller during summer measurements. The average nutrient loads (kg/d) for COD, BOD, SS, total P and total N were 48%, 17%, 33%, 7%, and 1% lower during the summer measurements compared to the spring measurements, respectively. The removal-% for COD, BOD, SS and total P differed at maximum 0.8% between the measurement periods. The removal-% of total N was 5000% higher during the summer campaign, because of denitrification. The effluent total N load (kg/d) was 58% smaller during the summer measurement campaign. The alkalinity of the inflow was 62% higher and the water temperature was 88% higher during the summer measurements.

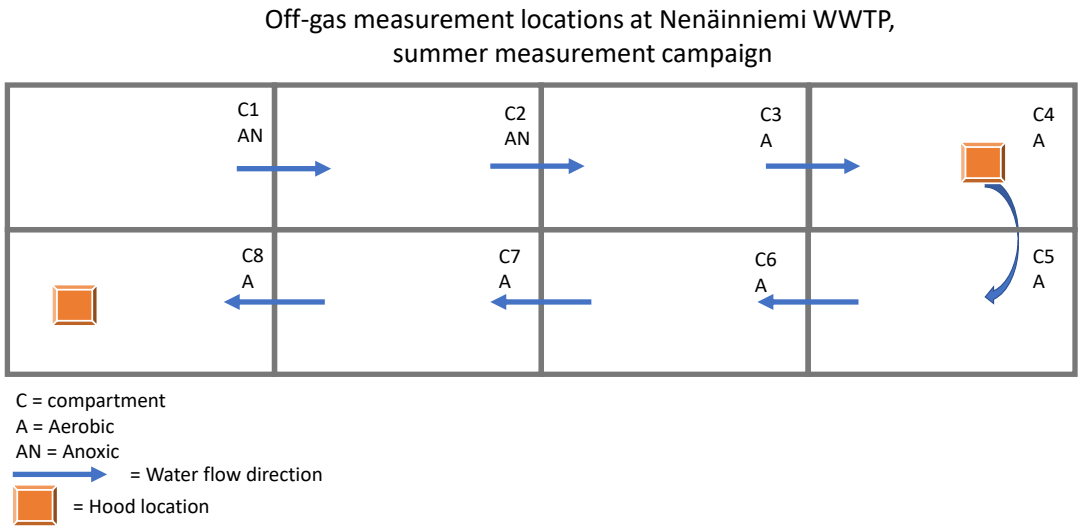


Figure 12: N_2O off-gas measurement locations at Nenäinniemi WWTP summer measurement campaign.

4 Results

4.1 Kakolanmäki WWTP spring measurement campaign

Figure 13 shows the off-gas N_2O concentration at Kakolanmäki WWTP compartment 6 line 2 during the spring measurement campaign. The average measured off-gas N_2O concentration was 0.47 g/Nm^3. The minimum concentration was 0.15 g/Nm^3, which accounts for 32% of the average. The maximum concentration was 0.77 g/Nm^3, which accounts for 165% of the average. Diurnal variation can be observed in the off-gas N_2O concentration (Figure 14). The lowest N_2O concentrations occurred between 8 AM and 11 AM and the highest concentrations between 4 PM and 12 AM.

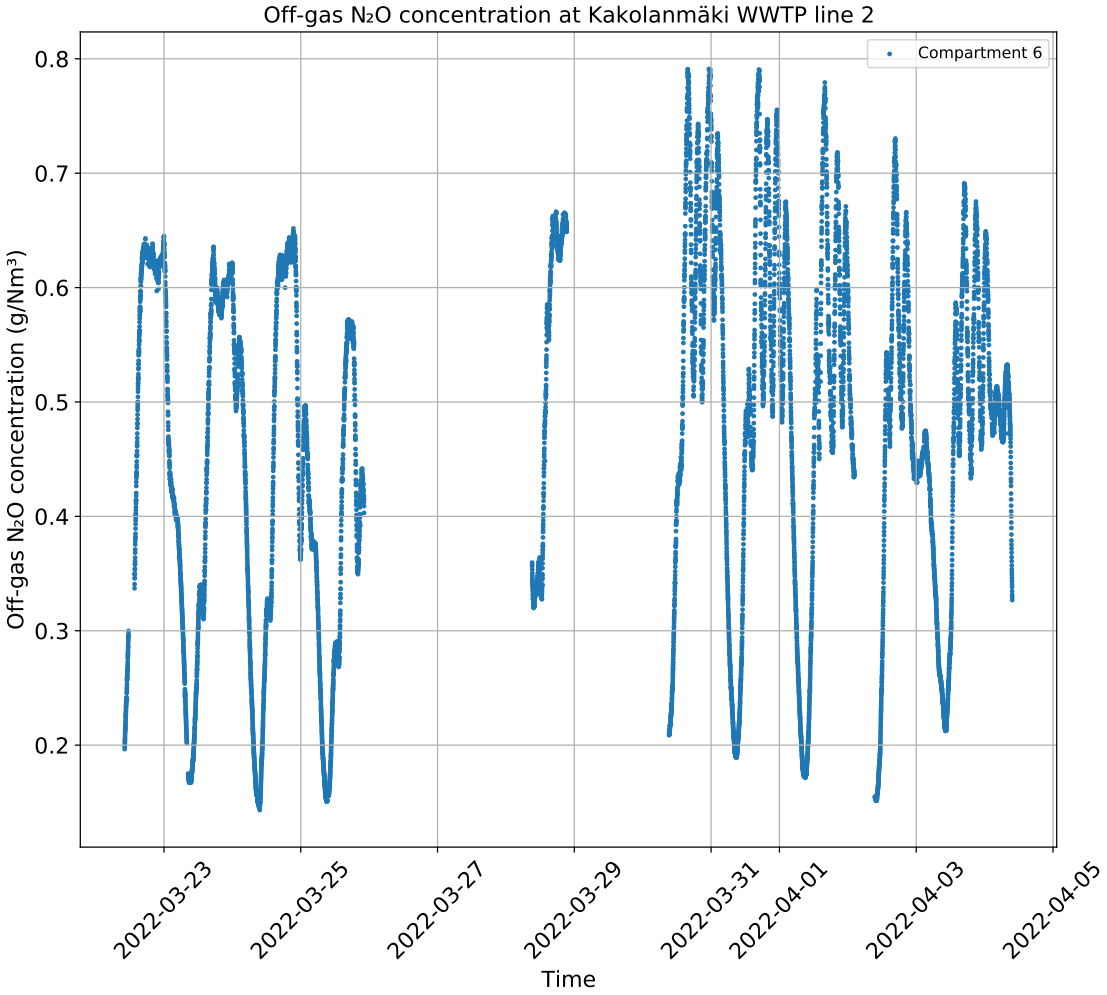
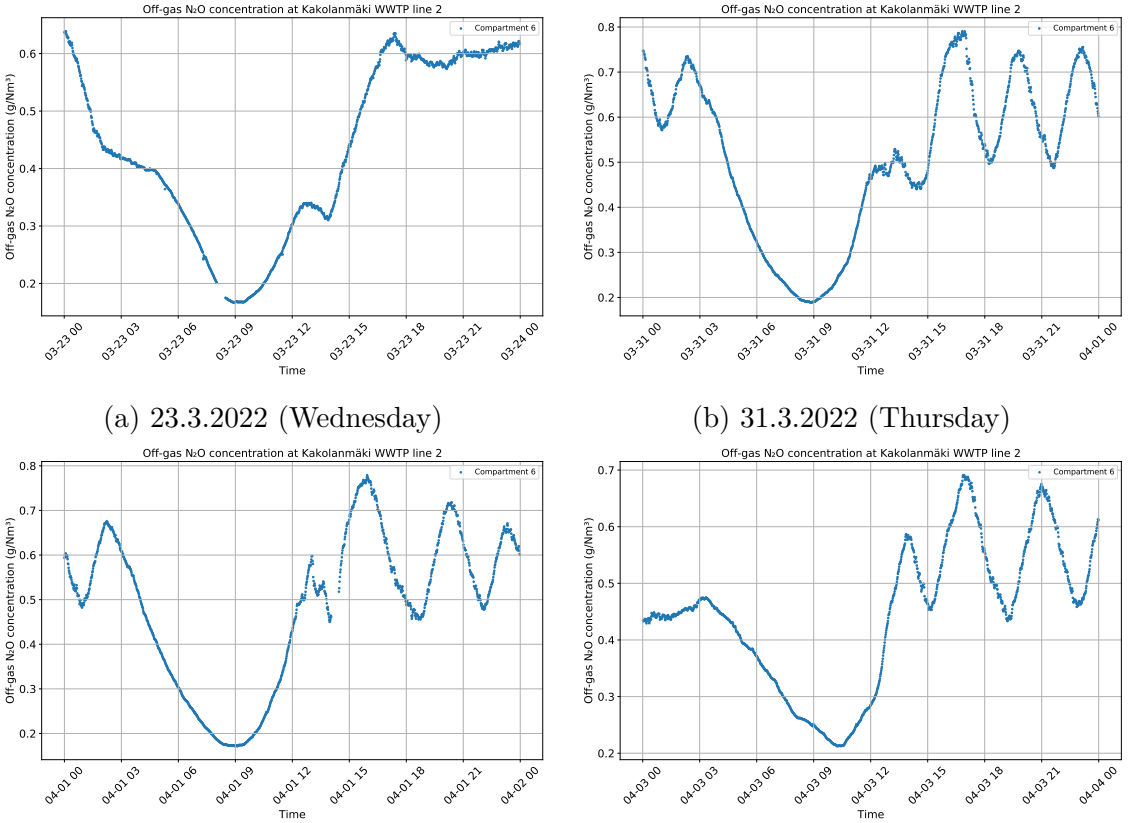


Figure 13: Off-gas N_2O concentration at Kakolanmäki WWTP during the spring measurement campaign.



(a) 23.3.2022 (Wednesday)

(b) 31.3.2022 (Thursday)

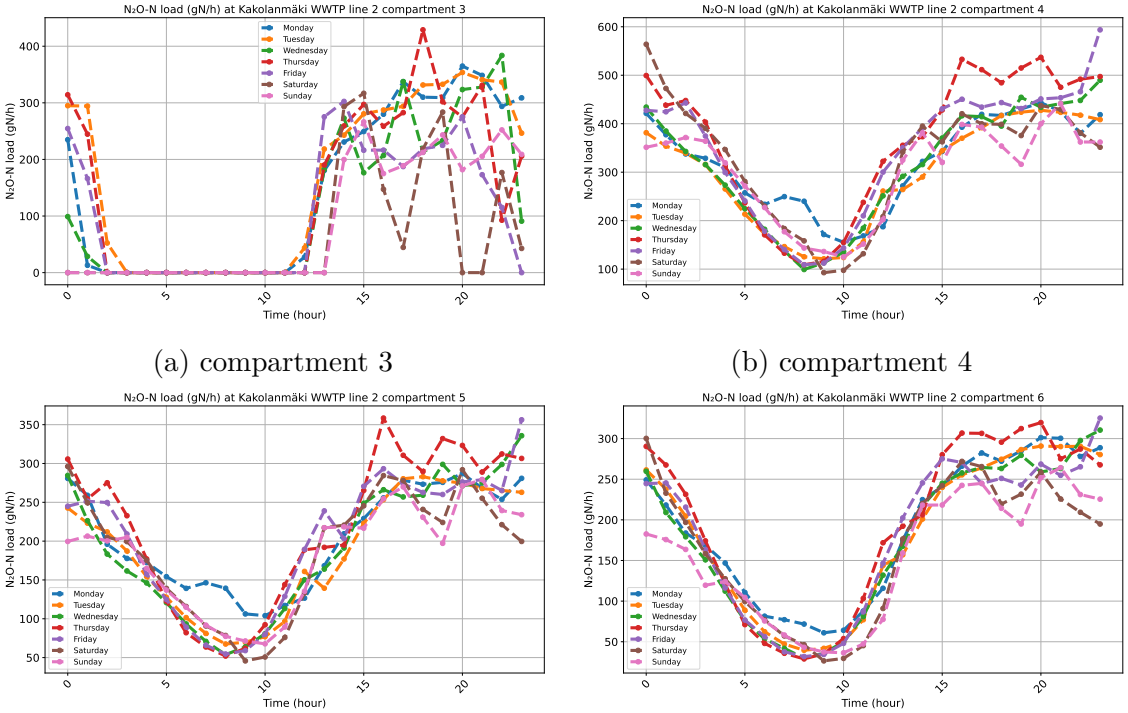
(c) 1.4.2022 (Friday)

(d) 3.4.2022 (Sunday)

Figure 14: Diurnal variation of the off-gas N_2O concentration at Kakolanmäki WWTP during the spring measurement campaign.

The off-gas N_2O concentration was measured successfully only from compartment 6 of line 2. In order to estimate the nitrous oxide emissions of the entire activated sludge process, off-gas N_2O concentrations in all the aerated compartments of the plant are assumed to be equal to the measured off-gas concentrations from compartment 6 of line 2. The validity of this assumption is addressed in the Discussions section. Based on this homogeneity assumption, the N_2O-N load (gN/h) for all the four aeration lines of Kakolanmäki can be estimated by multiplying N_2O-N concentration (gN/Nm^3) by hourly aeration volumes (Nm^3/h) of each aerated compartment of all the lines.

Figure 15 shows the hourly average N_2O-N load in all the aerated compartments of line 2. Because the off-gas N_2O-N concentration is assumed equal in all the compartments, the differences in N_2O-N load arise from differences in aeration. The third compartment is intermittently aerated, which leads to zero N_2O-N load during anoxic periods. The fourth compartment is most heavily aerated, leading to the largest N_2O-N loads. Similar patterns in aeration and N_2O-N load can be observed in Lines 1, 3, and 4 (data not presented).



(a) compartment 3

(b) compartment 4

(c) compartment 5

(d) compartment 6

Figure 15: N_2O-N load at Kakolanmäki WWTP line 2 during the spring measurement campaign.

The total N_2O-N load of Kakolanmäki was calculated as a sum of the N_2O-N loads of all the four aeration lines. Figure 16 presents the hourly average N_2O-N loads for every day of the week during the spring measurement period. The average of the hourly averages was equal to 3 154 gN/h during the measurement period. Maximum N_2O-N load was equal to 5 927 gN/h, which accounts for 187 % the average, and minimum N_2O-N load was equal to 643 gN/h, which accounts for 20 % of the average. The N_2O-N load exhibited similar diurnal variation to the off-gas N_2O concentration, with lowest values measured between 8 AM and 10 AM and highest between 4 PM and 11 PM.

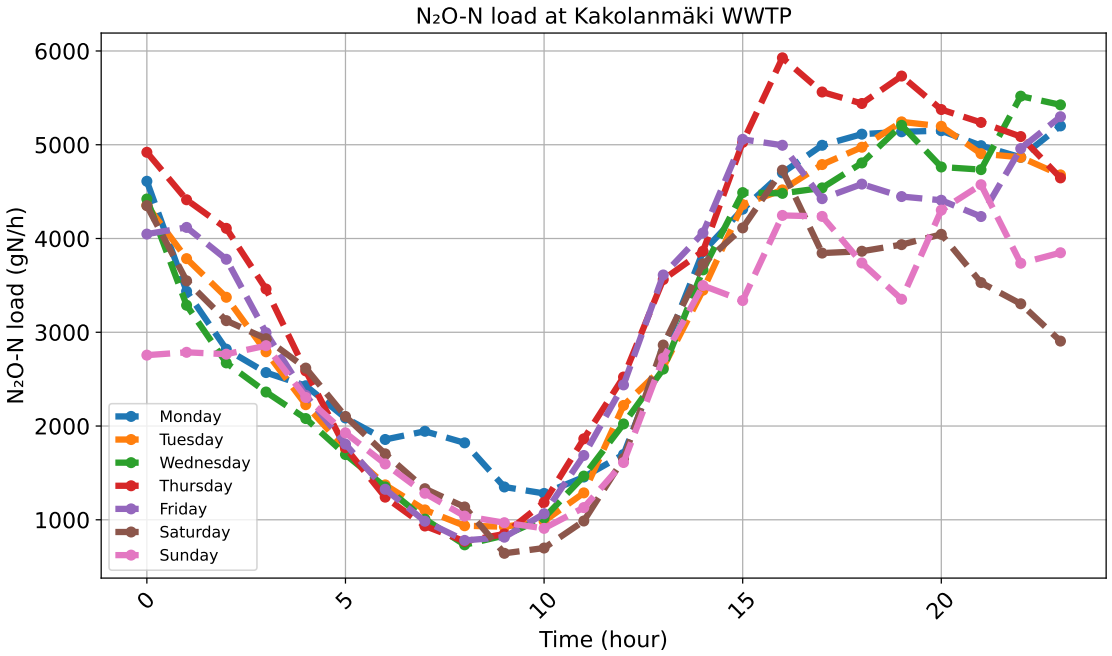
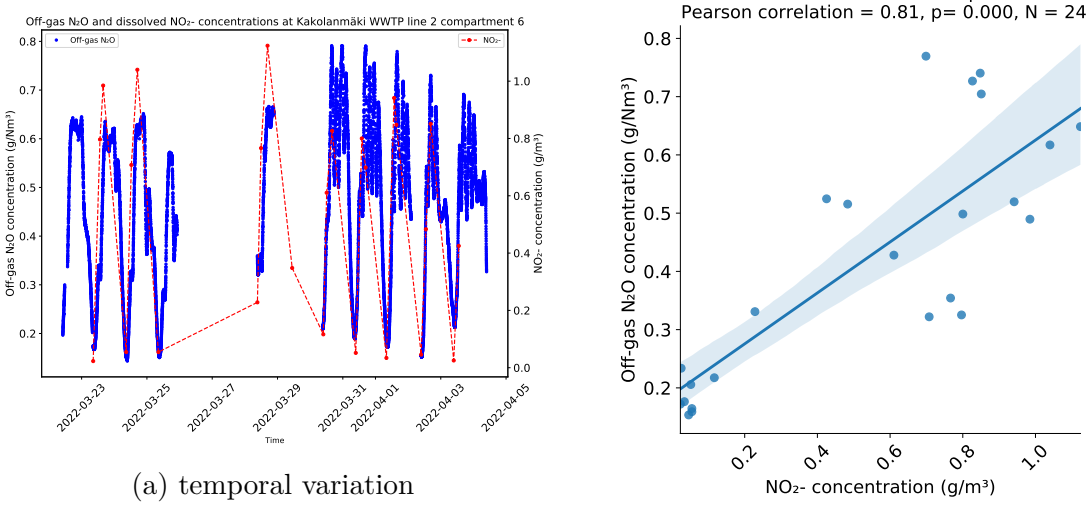


Figure 16: Hourly average N_2O-N load of Kakolanmäki WWTP during spring measurement campaign. The load calculation is based on compartment 6 line 2 off-gas concentrations and aeration data from all compartments.

The average EF for Kakolanmäki during the spring measurement campaign was equal to 1.7% of the influent N load. The median EF was equal to 1.8%. The emission factor was calculated by dividing the average or median N_2O-N load calculated from data shown in Figure 16 with an average or median influent nitrogen load of the plant during the measurement campaign. The average share of the nitrous oxide nitrogen from the removed total nitrogen was equal to 1.9%, and the median share of the nitrous oxide nitrogen from the removed total nitrogen was equal to 2.1%.

Additionally, the correlation between nitrous oxide emissions and dissolved nitrite concentrations was studied. The Pearson correlation between off-gas N_2O and dissolved NO_2^- was equal to 0.81 ($p = 1.33e-6$, N= 24) at Kakolanmäki WWTP line 2 compartment 6. The dissolved nitrite concentration at compartment 6 varied between 0.02 mg/l and 1.1 mg/l. Figure 17 presents a) the temporal variation and b) the correlation between off-gas N_2O and dissolved NO_2^-.



(a) temporal variation

(b) correlation

Figure 17: Off-gas N_2O and dissolved NO_2^- at Kakolanmäki WWTP line 2 compartment 6 during the spring measurement campaign.

4.2 Nenäinniemi WWTP spring measurement campaign

Figure 18 shows the off-gas N_2O concentrations at Nenäinniemi WWTP compartments 1 and 8, line D during the spring measurement campaign. The average N_2O concentration at compartment 1 was 0.13 g/Nm^3. The minimum N_2O concentration at compartment 1 was 0.040 g/Nm^3, which accounts for 31% of the average. The maximum N_2O concentration at compartment 1 was 0.35 g/Nm^3, which accounts for 273% of the average. Diurnal variation could be observed in the off-gas N_2O concentration of compartment 1. The lowest N_2O concentrations occurred between 10 AM and 4 PM and the highest between 12 AM and 4 AM (Figure 19).

The average measured off-gas N_2O concentration at compartment 8 was 0.18 g/Nm^3. The minimum concentration at compartment 8 was 0.048 g/Nm^3, which is equal to 27% of the average. The maximum concentration at compartment 8 was 0.58 g/Nm^3, which is equal to 326% of the average. Diurnal variation could be observed in the off-gas N_2O concentration of compartment 8. The lowest N_2O concentrations occurred between 9 AM and 12 PM and the highest between 9 PM and 2 AM (Figure 20).

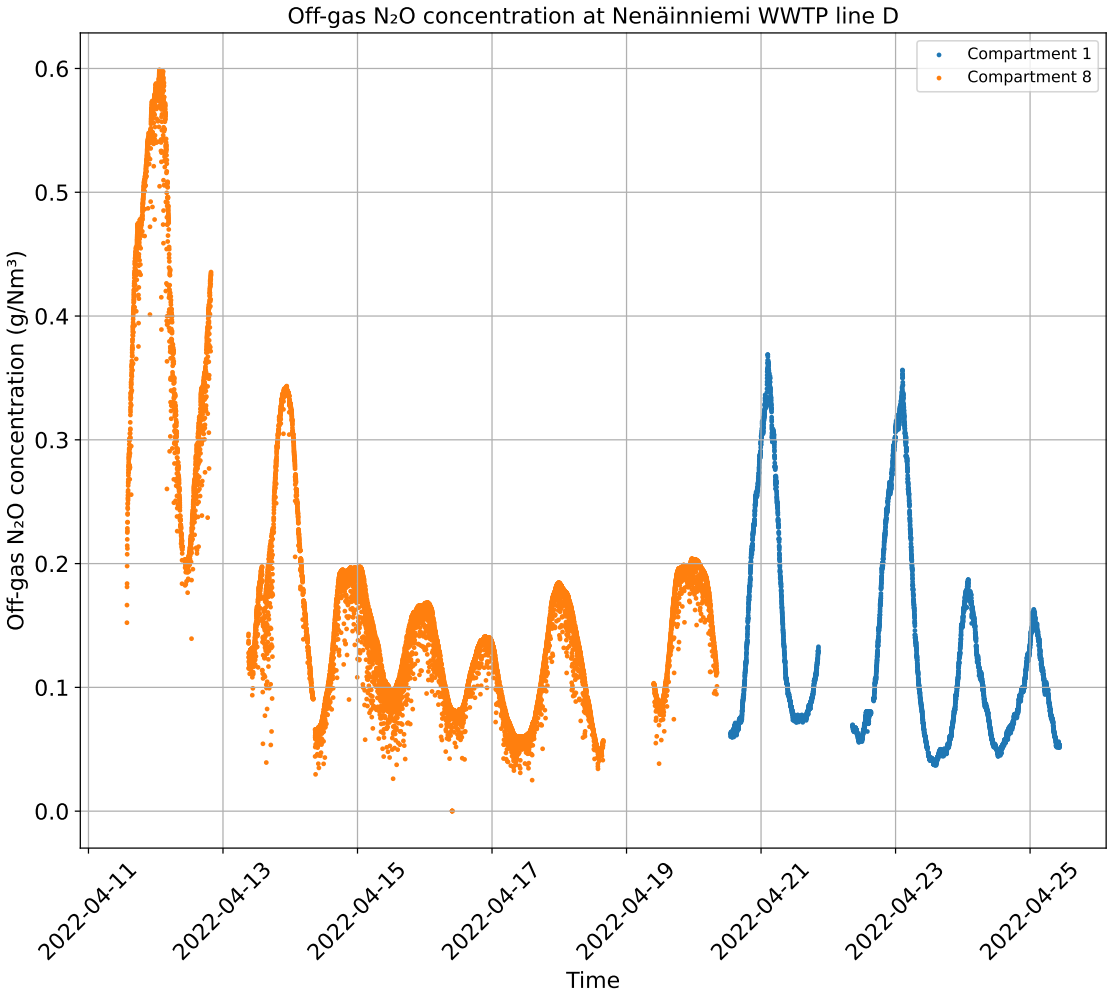
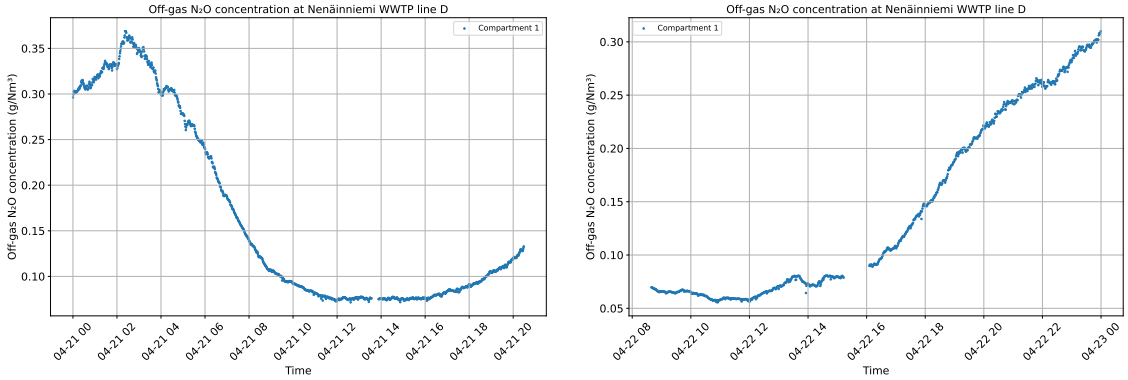
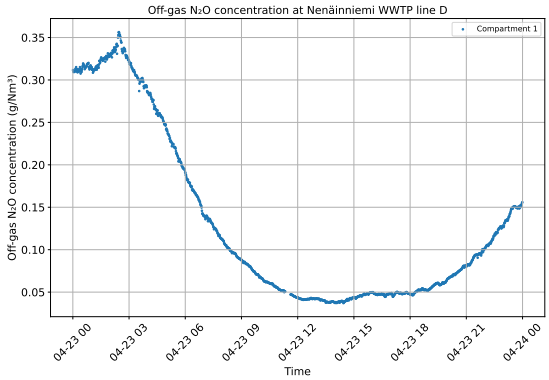


Figure 18: Off-gas N_2O concentration at Nenäinniemi during spring measurement campaign.

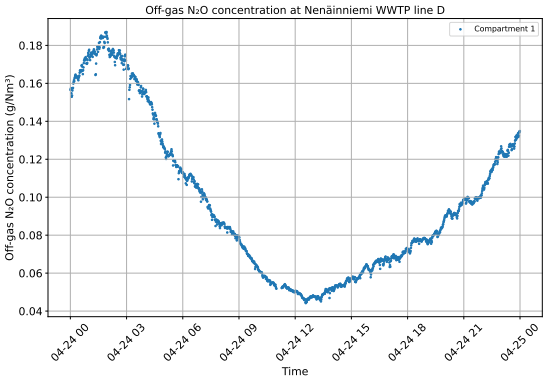


(a) 21.4.2022 (Thursday)

(b) 22.4.2022 (Friday)

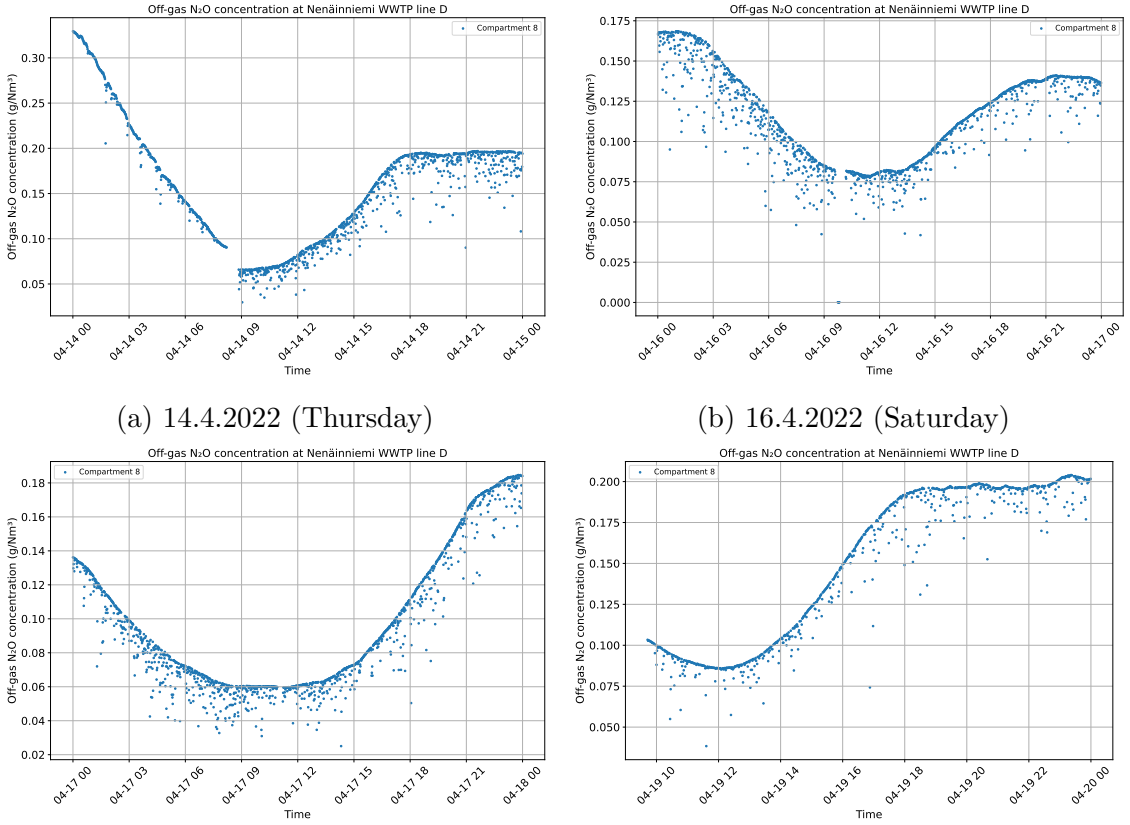


(c) 23.4.2022 (Saturday)



(d) 24.4.2022 (Sunday)

Figure 19: Diurnal variation of the off-gas N_2O concentration at Nenäinniemi WWTP compartment 1 during spring measurement campaign.



(a) 14.4.2022 (Thursday)

(b) 16.4.2022 (Saturday)

(c) 17.4.2022 (Sunday)

(d) 19.4.2022 (Tuesday)

Figure 20: Diurnal variation of the off-gas N_2O concentration at Nenäinniemi WWTP compartment 8 during the spring measurement campaign.

Off-gas N_2O concentrations of compartments that were not measured were estimated by linear regression from the data of the two measured compartments (compartments 1 and 8 from line D). The N_2O-N loads (gN/h) for all the aerated compartments were estimated by multiplying N_2O-N concentrations (gN/Nm^3) by hourly aeration volumes (Nm^3/h) of each compartment. During the spring measurement campaign, all the eight compartments of the aeration lines were constantly aerated.

The total N_2O-N load of Nenäinniemi was calculated as a sum of the N_2O-N loads of all the four aeration lines. Figure 21 presents the hourly average N_2O-N loads for every day of the week. The average N_2O-N load was equal to 1 583 gN/h. Maximum N_2O-N load was equal to 4 483 gN/h, which accounts for 283 % the average, and minimum N_2O-N load was equal to 482 gN/h, which accounts for 30 % of the average. The N_2O-N load exhibited diurnal variation with lowest values measured between 10 AM and 1 PM and highest between 11 PM and 2 AM.

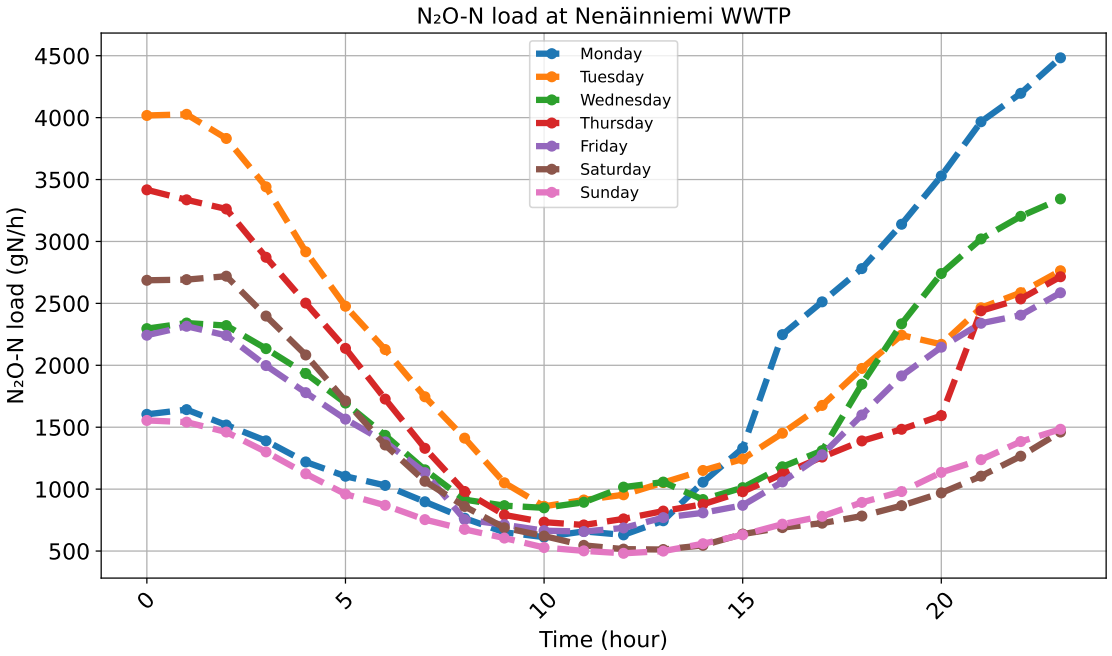
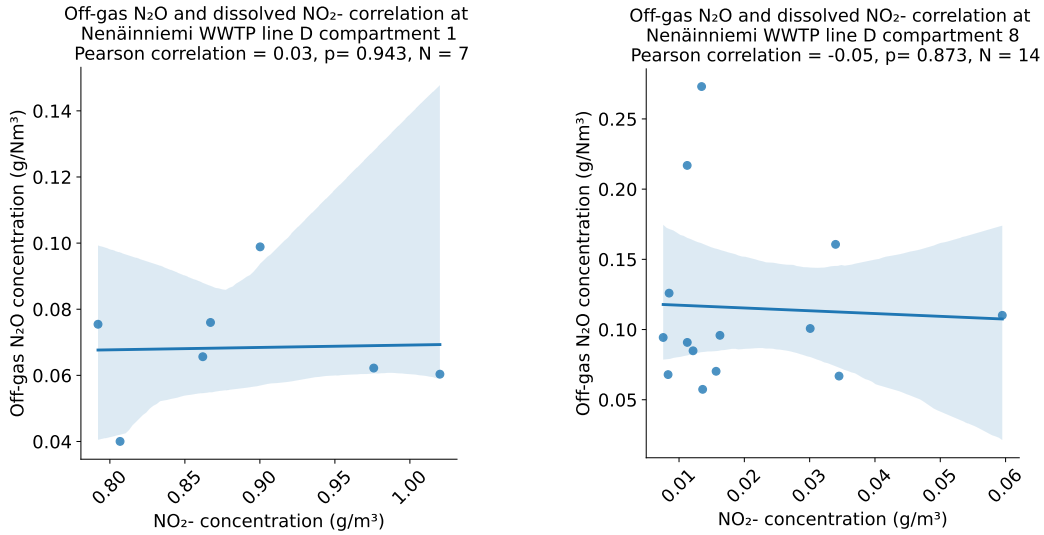


Figure 21: Hourly average N_2O-N load of Nenäinniemi WWTP during the spring measurement campaign. The load calculation is based on compartment 1 and 8 off-gas concentrations from line D and aeration data from all compartments and lines.

The average EF for Nenäinniemi during the spring measurement campaign was equal to 1.3% of the influent N load. The median EF was equal to 1.1%. The average share of the nitrous oxide nitrogen from the removed total nitrogen was equal to 28.0% and the median was equal to 23.9%.

No significant correlation between dissolved nitrite and off-gas nitrous oxide emissions was found in Nenäinniemi WWTP. The Pearson correlation between off-gas N_2O and dissolved NO_2^- was equal to 0.03 ($p = 0.943$, $N= 7$) at compartment 1 line D (Figure 22a) and -0.05 ($p = 0.873$, $N= 14$) at compartment 8 line D (Figure 22b). The dissolved nitrite concentration at compartment 1 varied between 0.8 mg/l and 1.1 mg/l. The dissolved nitrite concentration at compartment 8 varied between 0.008 mg/l and 0.06 mg/l. It should be noted that the sample sizes are rather small.



(a) Compartment 1

(b) Compartment 8

Figure 22: Off-gas N_2O and dissolved NO_2^- correlation at Nenäinniemi WWTP line D during the spring measurement campaign.

4.3 Kakolanmäki WWTP summer measurement campaign

Figure 23 shows the off-gas N_2O concentrations at compartments 4 and 6 from line 2 during the summer measurement period. The average measured N_2O concentration at compartment 4 was 0.014 g/Nm^3. The minimum N_2O concentration at compartment 4 was 0.003 g/Nm^3, which accounts for 22% of the average. The maximum N_2O concentration at compartment 4 was 0.059 g/Nm^3, which accounts for 432% of the average. Temporal variation can be observed in the off-gas N_2O concentration of compartment 4, but no clear repetitive pattern can be observed (Figure 24).

The average measured off-gas N_2O concentration at compartment 6 during the summer measurement campaign was $0.047 g/Nm^3$. The minimum concentration at compartment 6 was 0.0045 g/Nm^3, which accounts for 10% of the average. The maximum concentration at compartment 6 was 0.088 g/Nm^3, which accounts for 188% of the average. A recurring diurnal variation pattern could be observed in the off-gas N_2O concentration of compartment 6 (Figure 25). The lowest N_2O concentrations occurred between 7 AM and 11 AM and the highest between 3 PM and 11 PM.

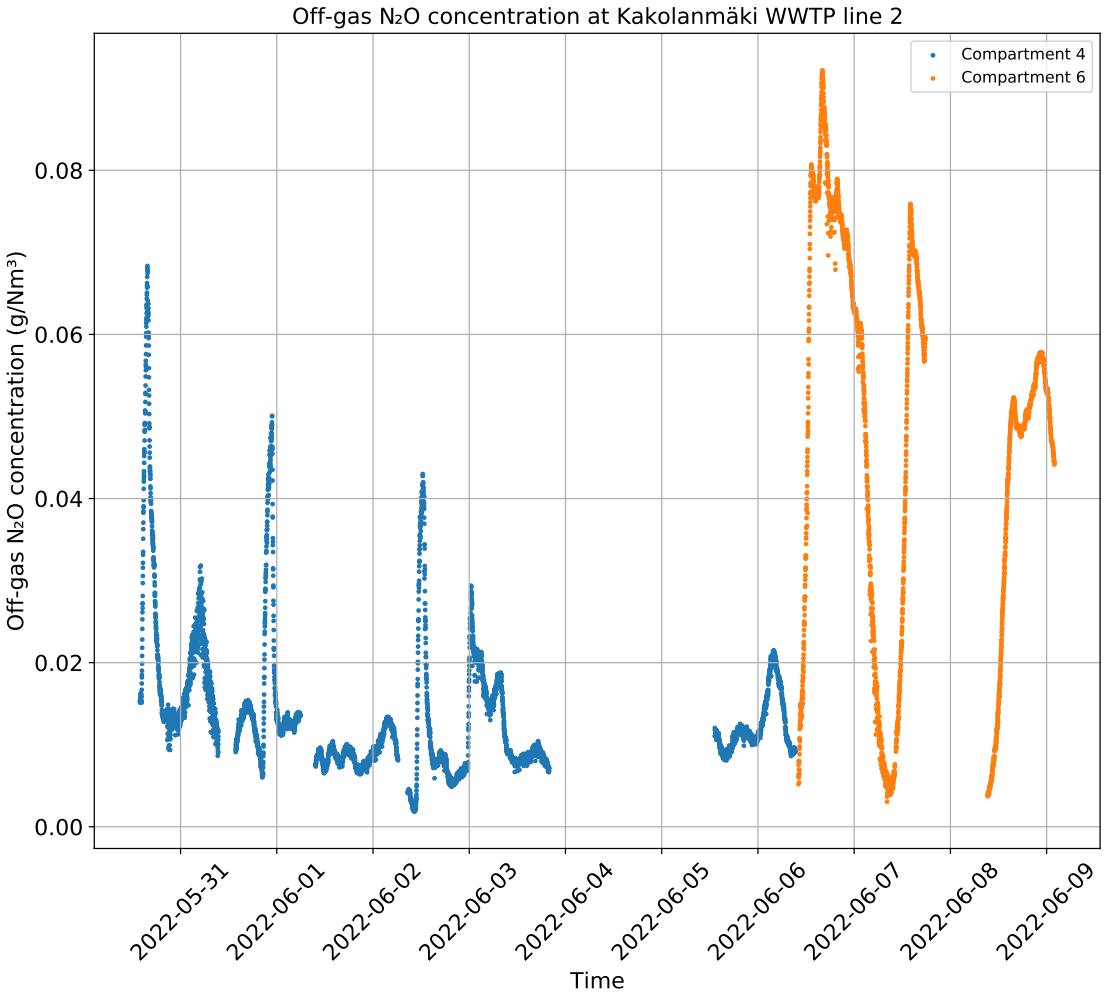
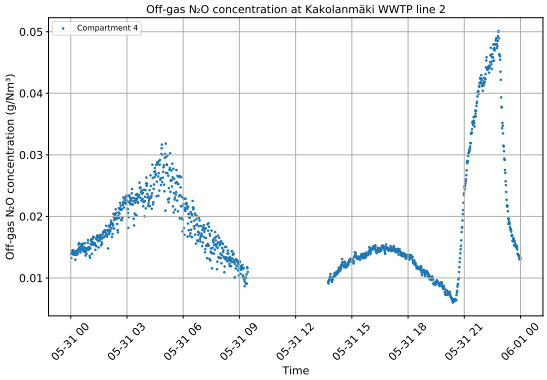
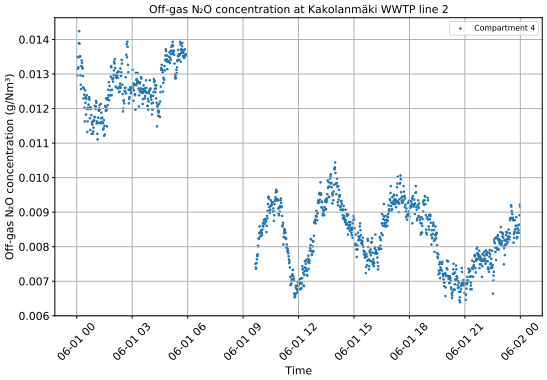


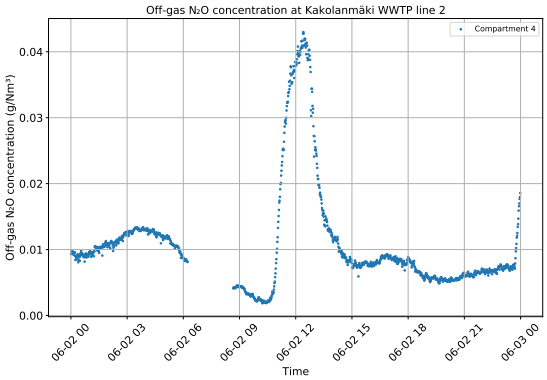
Figure 23: Off-gas N_2O concentration at Kakolanmäki during the summer measurement campaign.



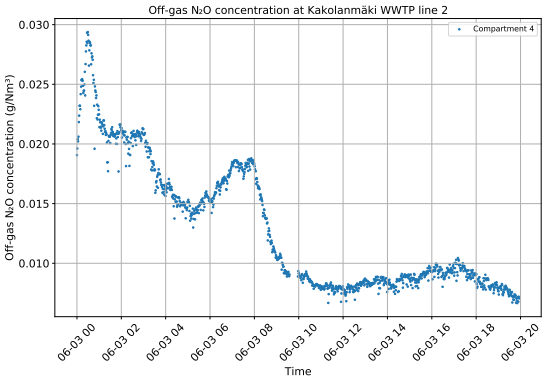
(a) 31.5.2022 (Tuesday)



(b) 1.6.2022 (Wednesday)

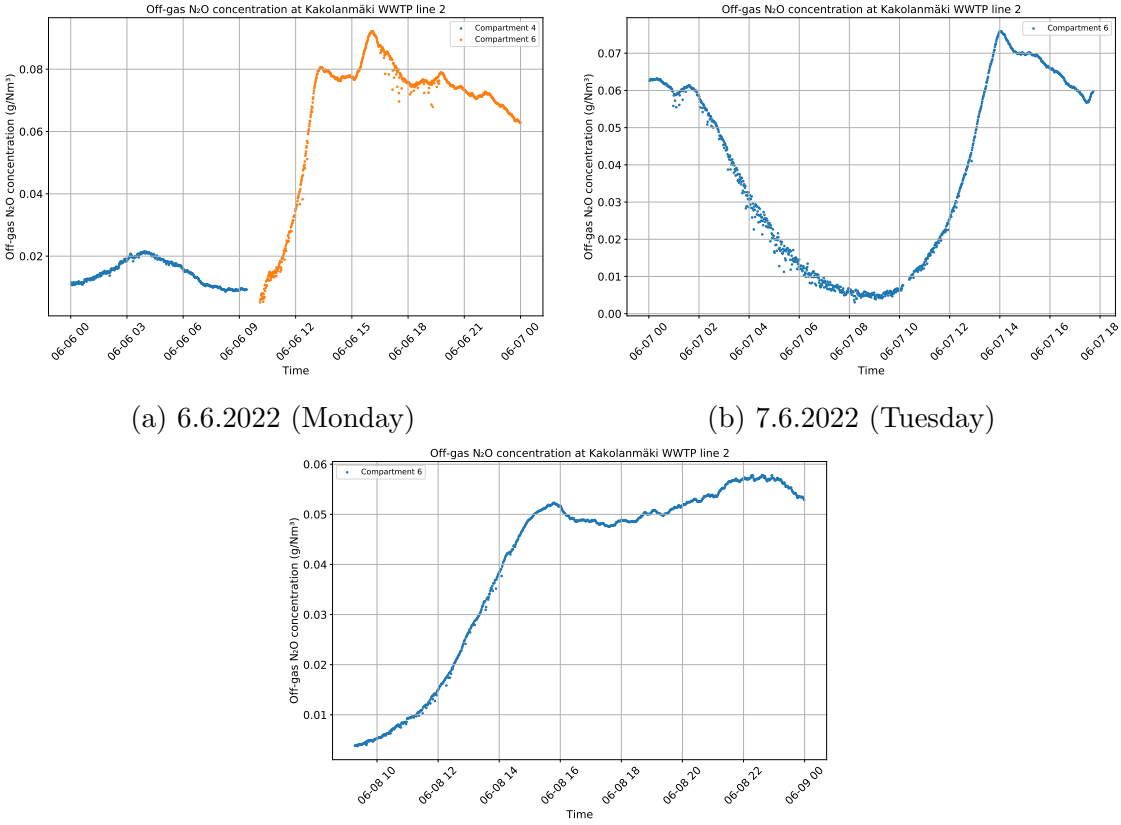


(c) 2.6.2022 (Thursday)



(d) 3.6.2022 (Friday)

Figure 24: Diurnal variation of the off-gas N_2O concentration at Kakolanmäki WWTP compartment 4 during the summer measurement campaign.



(a) 6.6.2022 (Monday)

(b) 7.6.2022 (Tuesday)

(c) 8.6.2022 (Wednesday)

Figure 25: Diurnal variation of the off-gas N_2O concentration at Kakolanmäki WWTP compartment 6 during the summer measurement campaign.

The off-gas N_2O concentrations of compartments that were not measured were estimated by linear regression from the data of the two measured compartments (compartments 4 and 6 from line 2). Figure 26 presents the hourly average N_2O-N loads of the plant for every day of the week. The average N_2O-N load was equal to 149 gN/h. Maximum N_2O-N load was 505 gN/h, which accounts for 338% the average, and minimum N_2O-N load was 23 gN/h, which accounts for 16% of the average. The N_2O-N load exhibited diurnal variation with lowest values measured between 8 AM and 10 AM and highest between 12 PM and 10 PM.

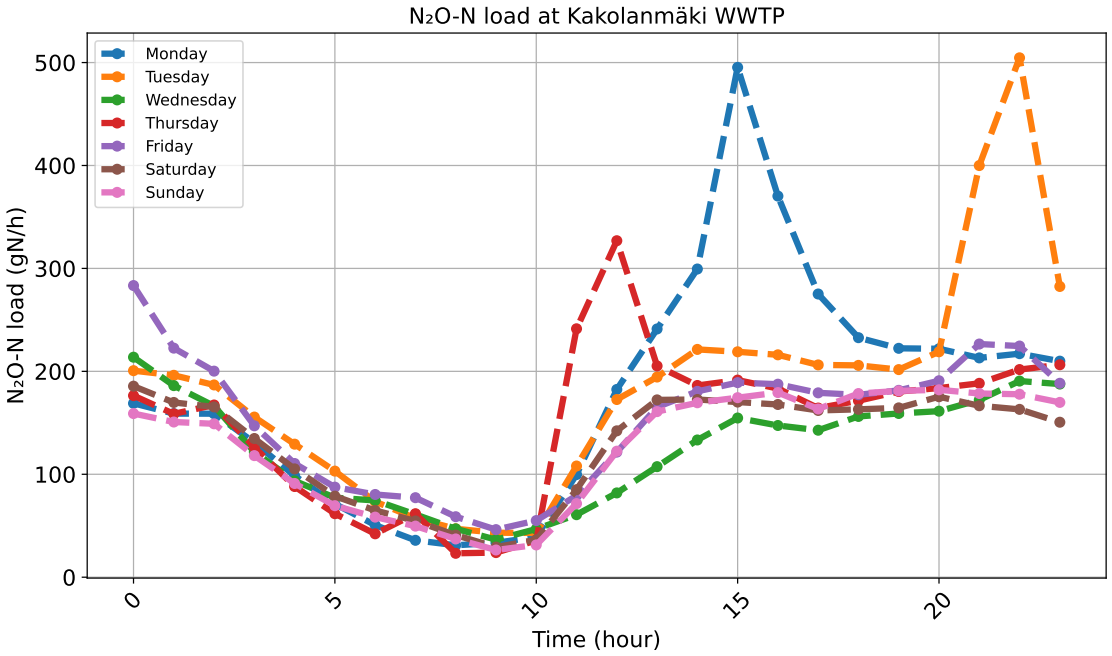


Figure 26: Hourly average N_2O-N load of Kakolanmäki WWTP during the summer measurement campaign. The load calculation is based on compartment 4 and 6 off-gas concentrations from line 2 and aeration data from all compartments and lines.

The average EF for Kakolanmäki WWTP during the summer measurement campaign was equal to 0.09% of the influent N load. The median EF was also equal to 0.09%. The average share of the nitrous oxide nitrogen from the removed total nitrogen was equal to 0.1%, and the median was also equal to 0.1%.

The Pearson correlation between off-gas N_2O and dissolved NO_2^- was equal to 0.99 ($p = 0.001$, $N= 5$) at Kakolanmäki WWTP line 2 compartment 4 and 0.97 ($p = 0.0051$, $N= 5$) at Kakolanmäki WWTP line 2 compartment 6. The dissolved nitrite concentration at compartment 4 varied between 0.1 mg/l and 0.3 mg/l. The dissolved nitrite concentration at compartment 6 varied between 0.01 mg/l and 0.2 mg/l. It should be noted that the sample sizes are small, and the dissolved nitrite concentrations were low at both compartments during the measurements.

4.4 Nenäinniemi WWTP summer measurement campaign

Figure 27 shows the off-gas N_2O concentrations at compartments 4 and 8 from line D during the summer measurement period. The average measured N_2O concentration at compartment 4 was 0.17 g/Nm^3. The minimum N_2O concentration at compartment 4 was 0.071 g/Nm^3, which accounts for 41% of the average. The maximum N_2O concentration at compartment 4 was 0.41 g/Nm^3, which accounts for 240% of the average. A diurnal variation pattern could be observed in the off-gas N_2O concentration of compartment 4 (Figure 28). The lowest N_2O concentrations occurred between 6 AM and 9 AM and the highest between 1 PM and 12 AM.

The average measured off-gas N_2O concentration at compartment 8 during the summer measurement campaign was 0.046 g/Nm^3. The minimum concentration at compartment 8 was 0.0027 g/Nm^3, which accounts for 6% of the average. The maximum concentration at compartment 8 was 0.13 g/Nm^3, which accounts for 288% of the average. A diurnal variation pattern could be observed in the off-gas N_2O concentration of compartment 8 (Figure 29). The lowest N_2O concentrations occurred between 8 AM and 10 AM and the highest between 7 PM and 10 PM.

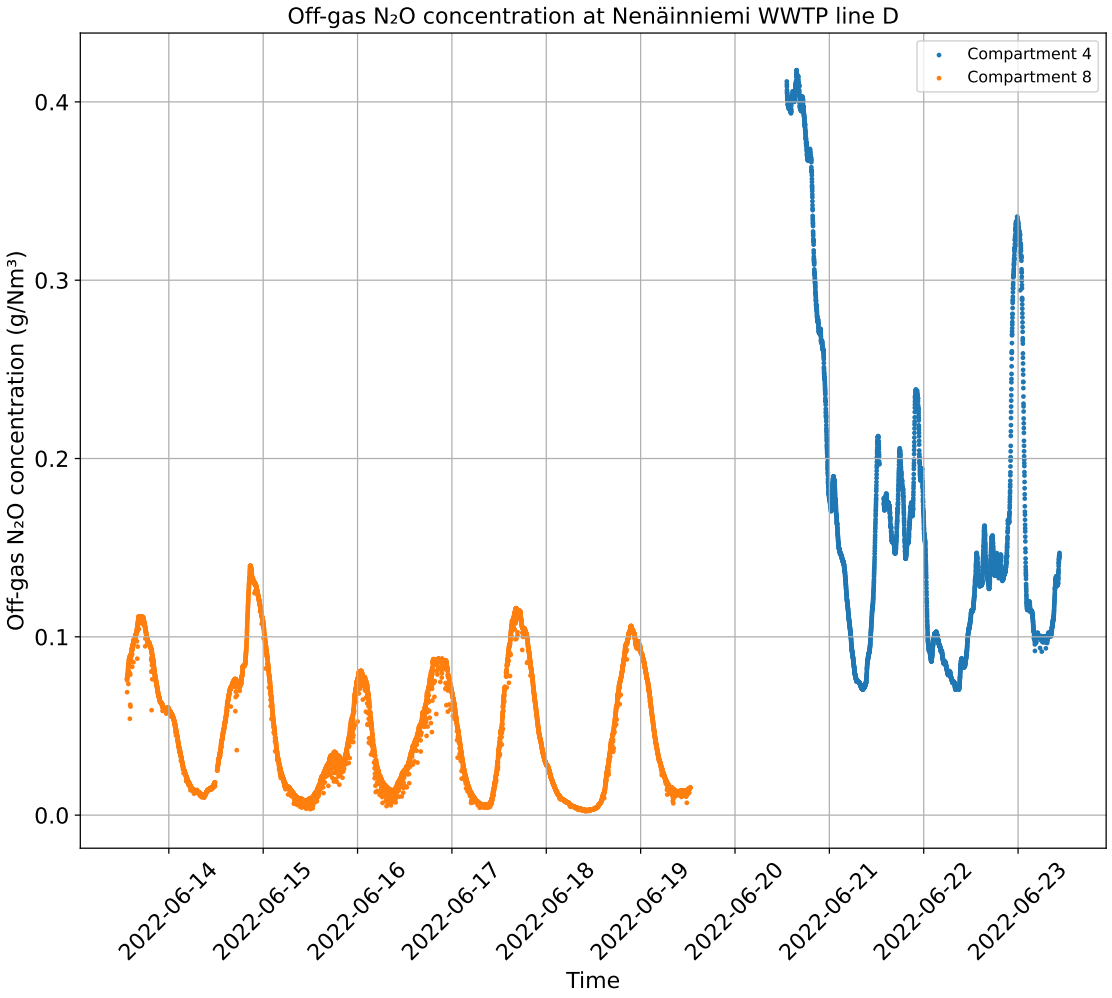
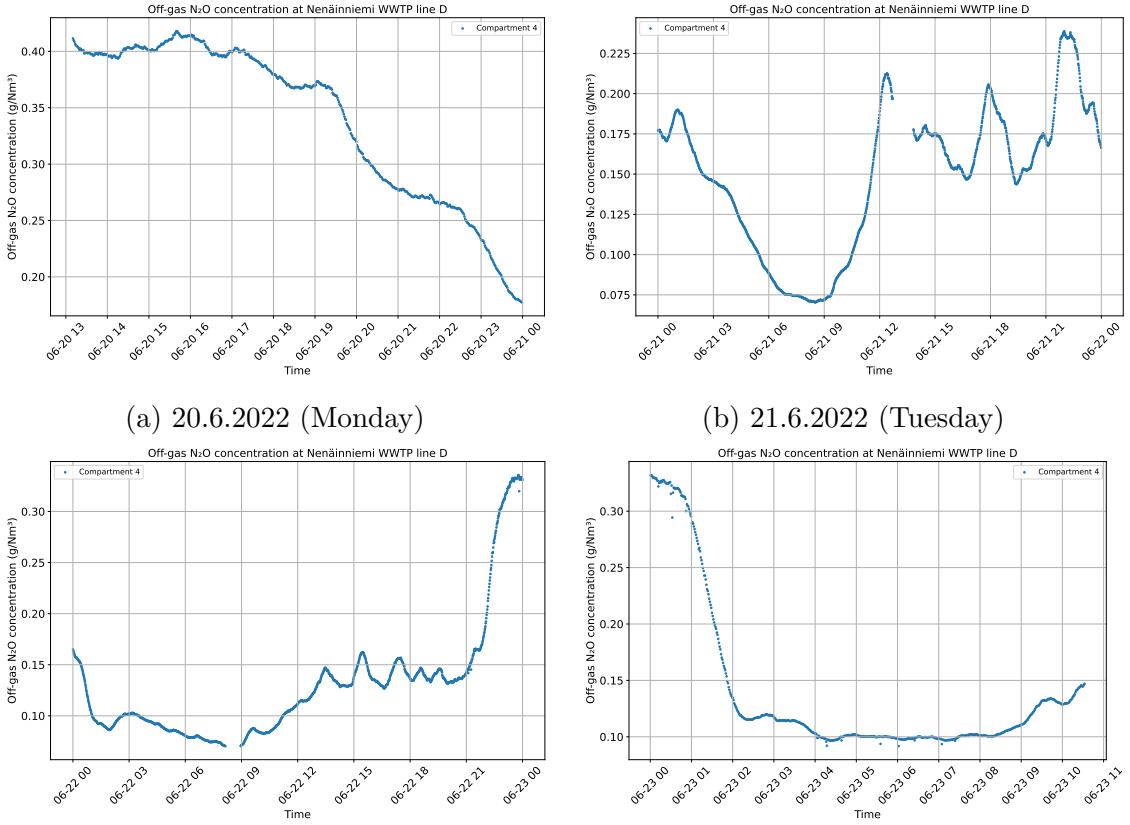


Figure 27: Off-gas N_2O concentration at Nenäinniemi WWTP during the summer measurement campaign.



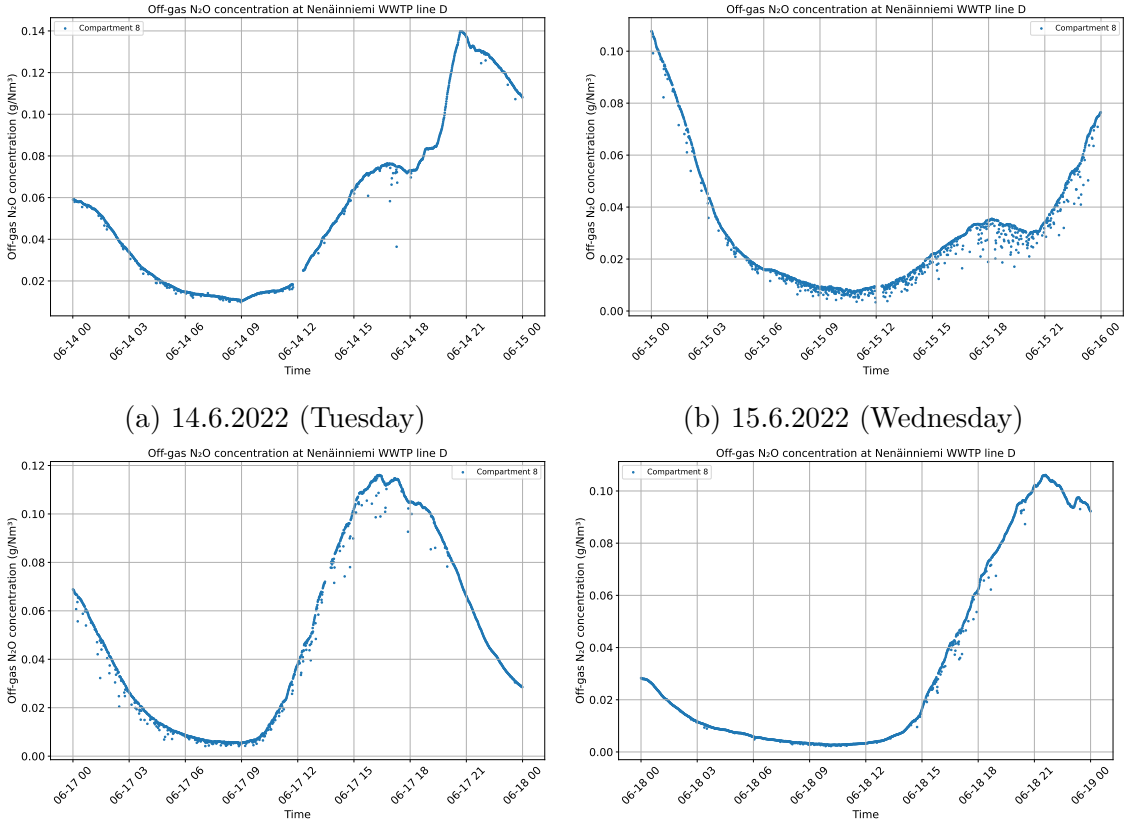
(a) 20.6.2022 (Monday)

(b) 21.6.2022 (Tuesday)

(c) 22.6.2022 (Wednesday)

(d) 23.6.2022 (Thursday)

Figure 28: Diurnal variation of the off-gas N_2O concentration at Nenäinniemi WWTP compartment 4 during the summer measurement campaign.



(a) 14.6.2022 (Tuesday)

(b) 15.6.2022 (Wednesday)

(c) 17.6.2022 (Friday)

(d) 18.6.2022 (Saturday)

Figure 29: Diurnal variation of the off-gas N_2O concentration at Nenäinniemi WWTP compartment 8 during the summer measurement campaign.

Off-gas N_2O concentrations of compartments that were not measured were estimated by linear regression from the data of the two measured compartments (compartments 4 and 8 from line D). The N_2O-N loads (gN/h) for all the aerated compartments were estimated by multiplying N_2O-N concentrations (gN/Nm^3) by hourly aeration volumes (Nm^3/h) of each compartment. During the summer measurement campaign, compartments from 3 to 8 of the aeration lines were constantly aerated.

The total N_2O-N load of Nenäinniemi was calculated as a sum of the N_2O-N loads of all the four aeration lines. Figure 30 presents the hourly average N_2O-N loads for every day of the week. The average N_2O-N load was equal to 1 161 gN/h. Maximum N_2O-N load was equal to 2 890 gN/h, which accounts for 249 % the average, and minimum N_2O-N load was equal to 313 gN/h, which accounts for 30 % of the average. The N_2O-N load exhibited diurnal variation with lowest values measured between 7 AM and 9 AM and highest between 11 PM and 12 AM.

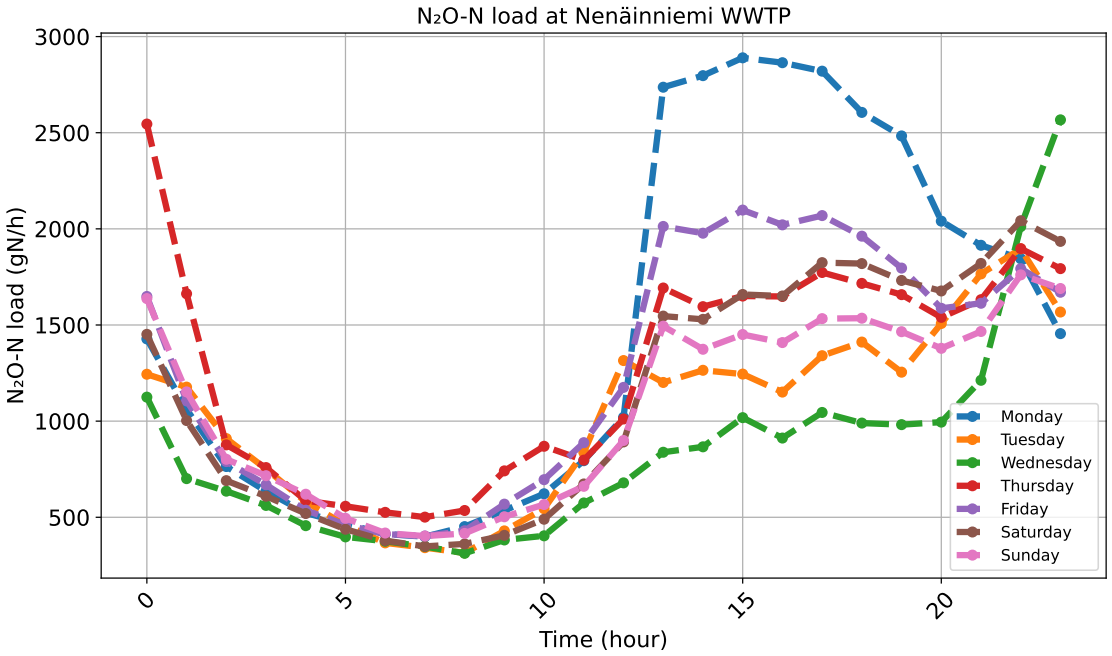


Figure 30: Hourly average N_2O-N load of Nenäinniemi WWTP during the summer measurement campaign. The load calculation is based on compartment 4 and 8 off-gas concentrations from line D and aeration data from all compartments and lines.

The average EF for Nenäinniemi during the summer measurement campaign was equal to 1.0% of the influent N load. The median EF was equal to 0.9%. The average share of the nitrous oxide nitrogen from the removed total nitrogen was equal to 1.7% and the median was equal to 1.5%.

No nitrite samples were collected from Nenäinniemi WWTP during summer measurement campaign due to time limitations.

4.5 Results based on all the data from Kakolanmäki WWTP and Nenäinniemi WWTP

Table 5 summarizes the results of the four measurement campaigns conducted in this thesis. General trends about the diurnal and the day of the week variation of the off-gas N_2O concentration can be observed if all the collected data from both Kakolanmäki WWTP and Nenäinniemi WWTP is combined. A clear diurnal pattern for the off-gas N_2O concentration can be observed from the combined data (Figure 31). The lowest off-gas N_2O concentrations occur 8–10 AM with an average value of 0.1 g/Nm^3. The highest concentrations occur 8–11PM, with an average value of 0.25 g/Nm^3, which is 250% of the minimum.

Table 5: Summary of results from Kakolanmäki WWTP and Nenäinniemi WWTP.

	Kakolanmäki (21.3.-4.4.2022)	Nenäinniemi (11.4.-25.4.2022)	Kakolanmäki (30.5.-9.6.2022)	Nenäinniemi (13.6.-23.6.2022)
Measurement locations	line 2 compartment 6	line D compartments 1 & 8	line 2 compartments 4 & 6	line D compartments 4 & 8
avg. EF (% of incoming total N)	1.7	1.3	0.09	1
avg. EF (% of removed total N)	1.9	28	0.1	1.7
avg. N2O-N load (gN/h)	3154	1583	149	1161
avg. N2O concentration (g/Nm3)	Compartment 6: 0.47	Compartment 1: 0.13 Compartment 8: 0.18	Compartment 4: 0.014 Compartment 6: 0.047	Compartment 4: 0.17 Compartment 8: 0.046
Min N2O concentration (% from average)	32%	Compartment 1: 31% Compartment 8: 27%	Compartment 4: 22% Compartment 6: 10%	Compartment 4: 41% Compartment 8: 6%
Max N2O concentration (% from average)	165%	Compartment 1: 273% Compartment 8: 326%	Compartment 4: 432% Compartment 6: 188%	Compartment 4: 240% Compartment 8: 288%
N2O correlation with nitrite	0.81 (p=0, N=24)	Compartment 1: 0.03 (p=0.9, N =7) Compartment 8: -0.05 (p =0.873, N =14)	Compartment 4: 0.99 (p=0.001, N =5) Compartment 6: 0.97 (p =0.005, N =5)	No data
Diurnal Max	4 PM-12AM	Compartment 1: 12-4AM Compartment 8: 9 PM-2AM	Compartment 4: not clear Compartment 6: 3-11PM	Compartment 4: 1PM-12 AM Compartment 8: 7 PM-10PM
Diurnal Min	8-11 AM	Compartment 1: 10 AM - 4PM Compartment 8: 9 AM- 12PM	Compartment 4: not clear Compartment 6: 7-11 AM	Compartment 4: 6-9 AM Compartment 8: 8-10 AM

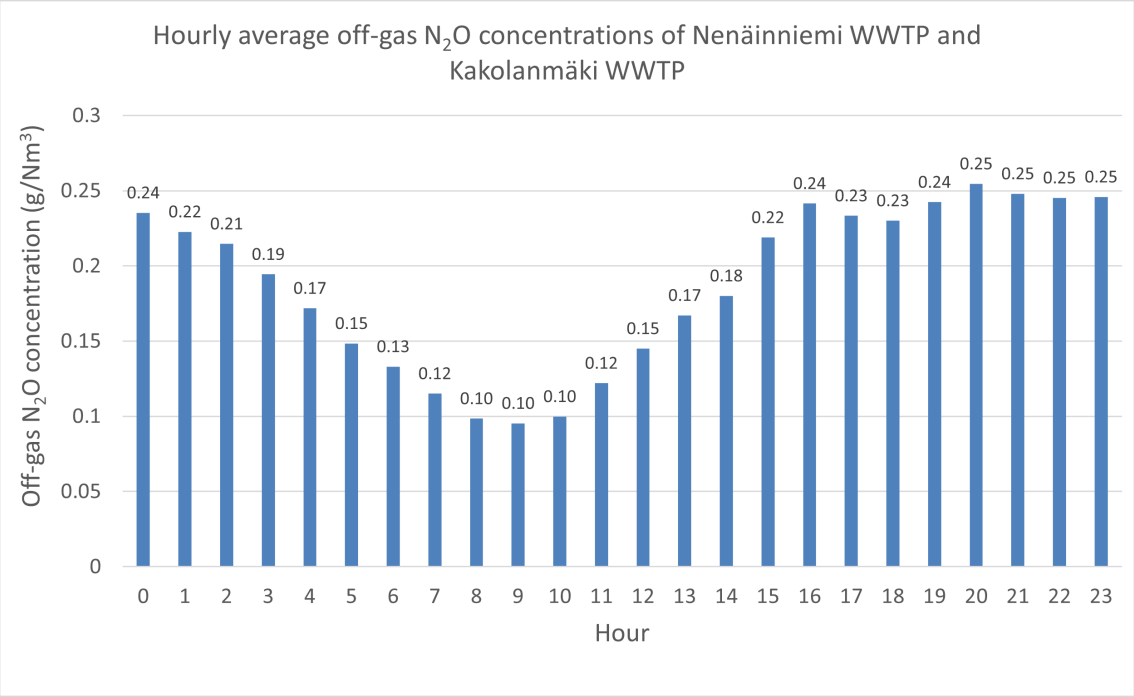


Figure 31: Hourly average off-gas N_2O concentrations calculated from all the collected data from Kakolanmäki WWTP and Nenäinniemi WWTP during spring and summer measurement campaigns.

Moderate differences between week and weekend off-gas N_2O concentrations can be observed (Figure 32). The lowest concentrations occur on average during Tuesdays with an average value equal to 0.16 g/Nm^3. The highest concentrations occur on average during Mondays and Thursdays with averages equal to 0.22 g/Nm^3. The maximum concentration is 36% higher than the minimum. The average concentration for Saturday and Sunday is 0.17 g/Nm^3. The shares of each compartment of each plant in the dataset are as follows: Kakolanmäki WWTP compartment 6: 30%, Kakolanmäki WWTP compartment 4: 13%, Nenäinniemi WWTP compartment 1: 12%, Nenäinniemi WWTP compartment 4: 8%, and Nenäinniemi WWTP compartment 8: 37%.

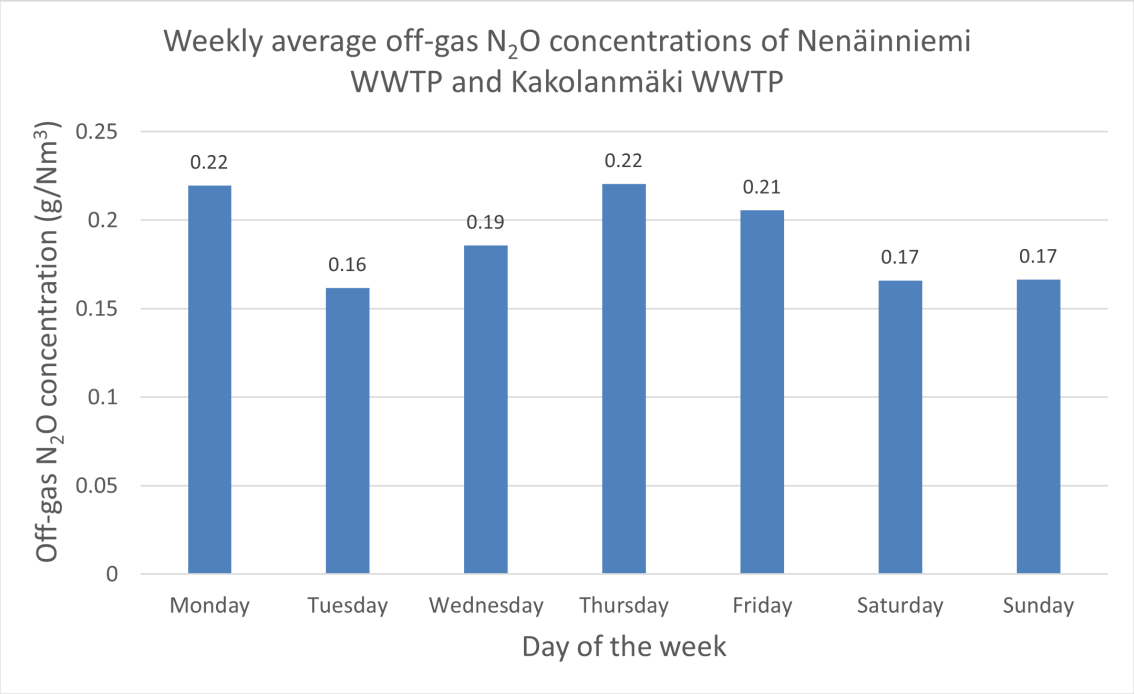


Figure 32: The day of the week average off-gas N_2O concentrations calculated from all the collected data from Kakolanmäki WWTP and Nenäinniemi WWTP during spring and summer measurement campaigns.

Moderate positive correlation between the dissolved nitrite and off-gas nitrous oxide can be found if the correlation is calculated for all the nitrite and nitrous oxide data from Kakolanmäki WWTP and Nenäinniemi WWTP (Figure 33). The Pearson correlation coefficient is equal to 0.57 with a p-value equal to 0, and number of samples equal to 55. The shares of each compartment of each plant in the dataset are as follows: Kakolanmäki WWTP compartment 6: 53%, Kakolanmäki WWTP compartment 4: 9%, Nenäinniemi WWTP compartment 1: 13%, and Nenäinniemi WWTP compartment 8: 25%. This result suggests moderate dependence between nitrous oxide emissions and dissolved nitrite. However, majority of the data is from compartment 6 of line 2 from Kakolanmäki WWTP.

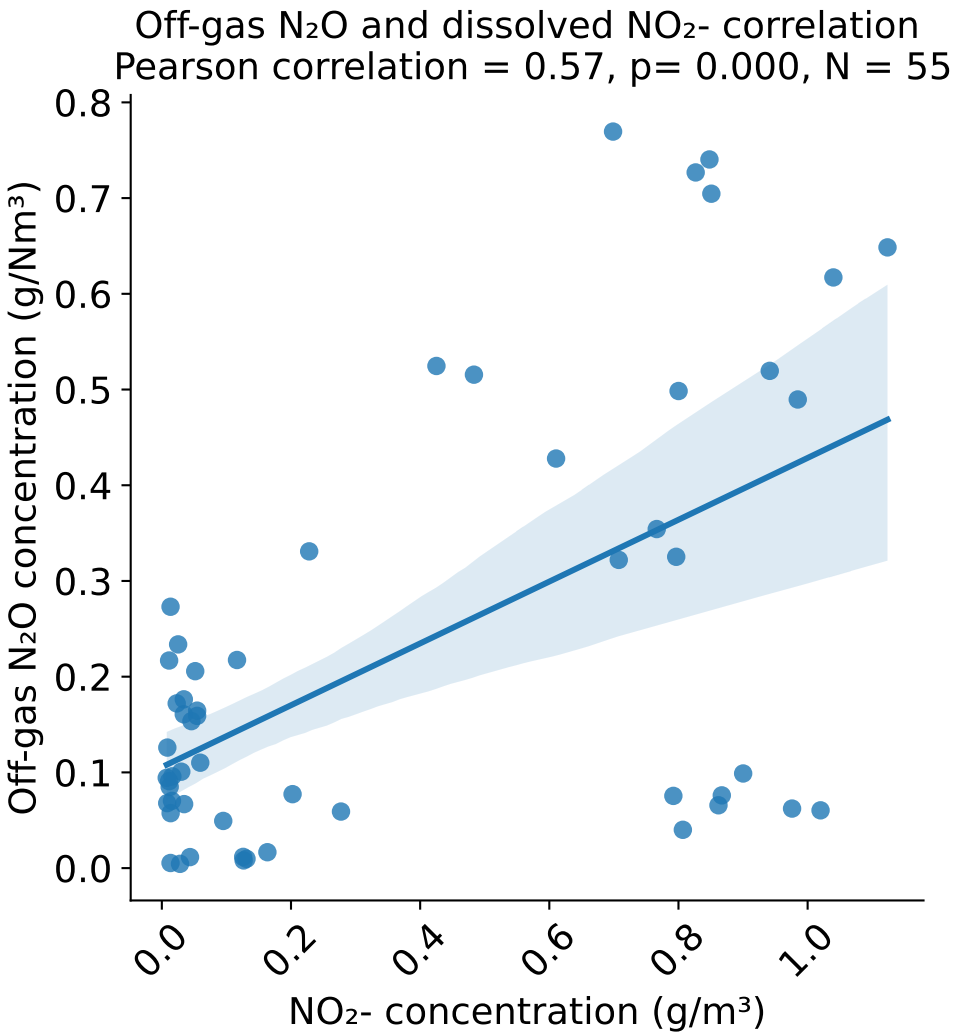


Figure 33: Off-gas N_2O and dissolved NO_2^- correlation calculated for all the collected data from Kakolanmäki WWTP and Nenäinniemi WWTP during spring and summer measurement campaigns.

4.6 Viikinmäki WWTP plant off-gas nitrous oxide emissions 2021-2022

Viikinmäki WWTP in Finland continuously measures off-gas N_2O emissions from plant exit gas. Off-gas N_2O data from Viikinmäki WWTP between 4.1.2021- 29.5.2022 was analyzed and daily emission factors were calculated for days in which incoming nitrogen concentration had been measured. In total, 139 daily emission factors were calculated for the 1.5-year period. These results from Viikinmäki WWTP are applied to compare the results of the short-term measurement campaigns conducted in this thesis against continuous long-term data. For a comprehensive presentation of Viikinmäki WWTP design and operation see for example the master's thesis papers by Myers (2019) and Kosonen (2013).

The daily emission factors from the analysis period are presented in Figure 34. The average daily emission factor in 2021 was equal to 1.2%. The minimum daily emission factor in 2021 was equal to 0.5% and the maximum was equal to 2.2%. The minimum daily emission factor accounts for 39% of the average while the maximum daily emission factor accounts for 193%. For the first half of 2022, the average emission factor equals 1.1%, minimum 0.04%, and maximum 2.6%. The minimum corresponds to 3% of the average while the maximum corresponds to 243%.

In Viikinmäki WWTP, during 2021 and early 2022, the daily emission factors varied from 3% of the annual average up to 243% of the annual average. If this would hold for Kakolanmäki WWTP and Nenäinniemi WWTP, and the average emission factors are studied, the Kakolanmäki WWTP daily emission factors could vary from 0.03% to 2.2%, and the Nenäinniemi WWTP daily emission factors could vary from 0.04% to 2.9%. However, this is highly speculative since the variance in the daily emission factors is process specific.

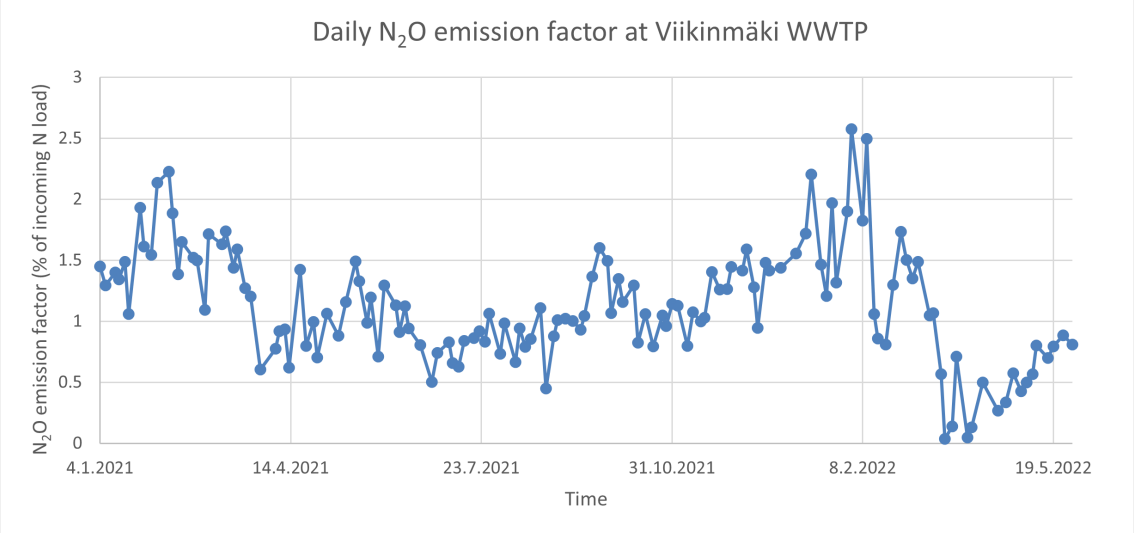
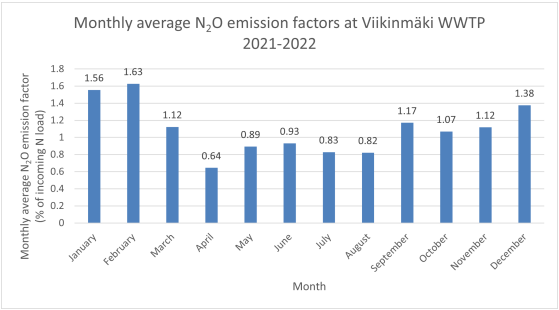


Figure 34: Daily N_2O emission factors at Viikinmäki WWTP.

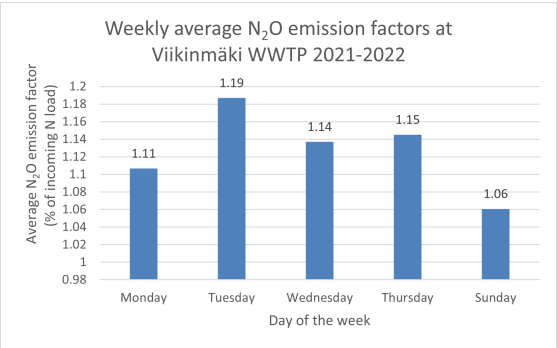
Figure 35a presents the monthly average emission factors of Viikinmäki WWTP during the analysis period. The results show that the emission factors are lowest during late spring and summer, from April to August. Between April and August, the average emission factor

falls below 1% while ranging between 1.6% and 1.1% during other months.

Figure 35b presents the day of the week average emission factors. Only part of the days are presented because incoming nitrogen data was limited to specific days. The results show that the emission factor is lowest during Sundays (1.06%) and highest on Tuesdays (1.19%). The maximum day of the week average is 12% higher than the minimum day of the week average.



(a) grouped by month



(b) grouped by day of the week

Figure 35: Average daily emission factors at Viikinmäki WWTP

5 Discussion

5.1 Dynamics of the off-gas nitrous oxide concentrations

Off-gas nitrous oxide concentrations exhibit temporal variation at Kakolanmäki WWTP and at Nenäinniemi WWTP, which is in line with the literature and data from Viikinmäki WWTP. The minimum concentrations at Kakolanmäki WWTP and Nenäinniemi WWTP accounted for 6-41% of the average concentrations while the maximum concentrations accounted for 165–432% (Table 5). Recurring diurnal patterns occurred except in compartment 4 of line 2 at Kakolanmäki WWTP. High off-gas N_2O concentrations at Kakolanmäki WWTP and at Nenäinniemi WWTP were observed between 1 PM and 4 AM and low concentrations between 7 AM and 4 PM. Furthermore, a clear diurnal pattern can be observed in the combined average off-gas data of all the measurement periods with the lowest off-gas N_2O concentrations occurring 8–10AM and the highest concentrations occurring 8–11PM (Figure 31). The high variance in the off-gas concentrations highlights the importance of continuous off-gas measurements. Discontinuous methods, such as grab samples would not likely capture the daily average concentration.

Moderate differences between the average off-gas N_2O concentrations of different days of the week can be observed (Figure 32). The maximum of the average day of the week concentrations was 36% higher than the minimum. This result is in line with Viikinmäki WWTP data, in which the maximum of the average day of the week emission factors was 12% higher than the minimum (Figure 35b).

The average off-gas N_2O concentration of a compartment varied between the measurement campaigns. At Kakolanmäki WWTP compartment 6 line 2, the average off-gas N_2O concentration was 0.47 g/Nm^3 during the spring campaign and 0.047 g/Nm^3 during the summer campaign. The summer campaign average accounts only for 10% of the spring campaign average. At Nenäinniemi WWTP, compartment 8 line D, the average off-gas N_2O concentration was 0.18 g/Nm^3 during spring campaign and 0.046 g/Nm^3 during summer campaign. The summer campaign average accounts for 26% of the spring campaign average. The Viikinmäki results from 2021 and 2022 also show seasonal variance in N_2O emission factors but no data about the off-gas concentrations of aeration compartments was studied. On average, the lowest N_2O emission factors occurred in April and highest in February (Figure 35a). The April average emission factor accounted for 40% of the February average emissions. In the literature it is also generally observed that nitrous oxide emissions exhibit seasonal variation (Vasilaki et al., 2019; Gruber et al., 2021b).

5.2 Correlation between the off-gas N_2O concentration and dissolved NO_2^-

At Kakolanmäki WWTP, strong positive correlation between the off-gas N_2O and the dissolved nitrite could be observed during both spring and summer measurement campaigns. It should be noted that during the summer measurement campaign the dissolved nitrite levels remained below 0.28 mg/l and 0.2 mg/l at compartments 4 and 6, respectively. These levels are low, and therefore the results from the summer do not show the effect of elevated nitrite concentrations on nitrous oxide.

No correlation was found in Nenäinniemi WWTP during spring measurements and no samples were taken during the summer measurement campaign. During the Nenäinniemi spring campaign, the dissolved nitrite level of compartment 1 was in the range of 0.8–1.1

mg/l. This rather constant nitrite level at the beginning of the aeration line is likely a consequence of the nitrite returning to the aeration line in the return activated sludge from the secondary clarifier. Most of the DO in the beginning of the aeration line is used to break down organic matter, and nitrification, that also requires DO, is not typically taking place in large quantities. Since nitrous oxide and nitrite observed at Nenäinniemi WWTP compartment 1 are likely recycled from secondary clarifier, no conclusions on the correlation on the production location of N_2O and nitrite can be made based on compartment 1 data.

During the Nenäinniemi spring campaign, the dissolved nitrite concentrations of compartment 8 were below 0.06 mg/l, and therefore the results do not show the effect of elevated nitrite concentrations on nitrous oxide. Additionally, the sample sizes available in the correlation analysis of individual measurement campaigns are rather small. Thus, longer sampling campaigns should be conducted to verify the correlation between nitrite and nitrous oxide in these plants.

Moderate positive correlation (Pearson correlation = 0.57) between the dissolved nitrite and off-gas nitrous oxide could be found if the correlation was calculated for all the nitrite and nitrous oxide data from Kakolanmäki WWTP and Nenäinniemi WWTP (Figure 33). However, it should be noted that 53% of the correlation data was collected from compartment 6 of line 2 from Kakolanmäki WWTP and is therefore biased towards that specific measurement location. The moderate correlation is in line with the literature. For example, Gruber et al. (2021b) found a moderate positive correlation equal to 0.65 between effluent nitrite concentration and N_2O emissions in a study of 14 long-term campaigns.

5.3 N_2O emission factors and emission mitigation

Emission factors exhibit temporal variation at Kakolanmäki WWTP and at Nenäinniemi WWTP, which is in line with data from Viikinmäki WWTP. The average EF at Kakolanmäki WWTP was 1.7% during spring campaign and 0.09% during summer campaign. The summer campaign EF accounts only 5% of the spring campaign emission factor. The average EF at Nenäinniemi WWTP was 1.3% during spring campaign and 1.0% during summer campaign. The summer campaign EF accounts 77% of the spring campaign emission factor. The temporal variation in emission factors is line with Viikinmäki WWTP results: the minimum emission factor in the first half of 2022 was 0.04% and accounted for 3% of the average EF of the first half of 2022 (Figure 35a).

At Kakolanmäki WWTP, the average inflow was 41% smaller and nutrient inflow concentrations were 50-83% larger during the summer measurement campaign compared to the spring campaign. However, the incoming nutrient loads (kg/d) were rather similar between the two measurement periods, with a maximum difference of 11%. The incoming nitrogen load was 10% lower during the summer measurements compared to the spring measurement, which could contribute to the lower emissions during summer measurements. Additionally, the COD load was 11% higher during the summer measurements, which allows higher COD to N ratio and more efficient denitrification, lowering N_2O emissions. Furthermore, the alkalinity of the influent was 28% higher during the summer measurement campaign. Negative correlation between N_2O emissions and alkalinity has been observed at Viikinmäki WWTP with lowest emission at alkalinity levels above 1.4 mmol/l (Kosonen, 2013). At Kakolanmäki WWTP, the average alkalinity of the wastewater in the secondary clarifier was 2 mmol/l during the spring measurement campaign, and 2.2 mmol/l during the summer measurement campaign. Both values are above the 1.4 mmol/l limit observed in Viikinmäki WWTP. Therefore, the difference in influent alkalinity between the measurement

periods does not alone explain the differences in the emissions.

The most notable difference between the measurement period process parameters at Kakolanmäki WWTP was in the water temperature. The average water temperature was 5.4 °C higher during the summer measurement period compared to the spring measurement period. This difference in water temperature could at least partly explain the smaller off-gas N_2O concentrations and the smaller emission factor during the summer measurement campaign compared to the spring campaign. Negative correlation between wastewater temperature and N_2O emissions has also been observed in Kralingseveer WWTP in the Netherlands (Daelman et al., 2013), but not in Viikinmäki WWTP in Finland (Kosonen et al., 2016).

During the summer measurement campaign at Kakolanmäki WWTP, the average dissolved oxygen concentrations at compartments 4 and 6 of line 2 were 1.8 mg/l and 1.4 mg/l, respectively. Massara et al. (2018) found an optimal aeration level between 1.8 and 2.5 mg/l with ASM2d-N_2O simulation model of a municipal anaerobic/anoxic/oxic (A2/O) WWTP with biological removal of organic matter, nitrogen and phosphorus. Therefore, the lower dissolved oxygen level at Kakolanmäki WWTP compartment 6 could partly contribute to the higher emissions compared to compartment 4. However, during the spring measurement campaign, the average compartment 6 off-gas N_2O concentration was 900% higher compared to the summer measurement campaign despite having an average DO level of 1.7 mg/l. This result shows the multivariate nature of nitrous oxide emissions: higher DO level does not necessary lead to lower emissions if other process parameters are not optimal.

The maximum dissolved nitrite concentration at Kakolanmäki WWTP compartment 6 was 1.1 mg/l during the spring campaign and 0.2 mg/l during the summer campaign. The high nitrite peaks during the spring campaign could also contribute to the elevated N_2O emissions, because elevated nitrite levels lead to increased AOB denitrification, leading to higher N_2O production (Chen et al., 2020). Thus, monitoring and mitigating nitrite accumulation is also a possible N_2O mitigation measure for Kakolanmäki WWTP. Increasing SRT could be tested as a nitrite accumulation mitigation measure, since longer SRT allows sufficient growth of NOB and ensures efficient nitrification (Kampschreur et al., 2008a).

As a conclusion, several possible N_2O mitigation measures could be pointed out for Kakolanmäki WWTP by comparing the differences in process parameters during spring and summer measurement campaigns: increasing the COD to N ratio, maintaining the compartment 6 DO concentration close to 1.8 mg/l, increasing the SRT during nitrite accumulation, and increasing the alkalinity. Research should be conducted to test the effectiveness of these strategies, and the trade-offs between GHG emissions, energy consumption and system performance should be considered.

At Nenäinniemi WWTP, the average daily inflow was 45% smaller during the summer measurement campaign compared to the spring measurement campaign. The water temperature was 6.8 degrees higher during summer measurements. The alkalinity of the incoming water was 62% higher during the summer measurements but the average alkalinity of the effluent was above 1.4 mmol/l during both campaigns. The most notable difference between the measurement periods was in the total nitrogen removal-%. The removal-% for total N increased 5000% from 1% to 59%.

Total nitrogen removal could be an effective N_2O mitigation measure at Nenäinniemi WWTP, since the emission factor was 23% lower during the measurement campaign conducted during denitrifying season. Plants with total nitrogen removal have on average lower

emission factors compared to plants with only nitrification as the treatment goal (Gruber et al., 2021b). However, the effect of denitrification on N_2O emissions at Nenäinniemi WWTP should be studied further to rule out the effect of water temperature increase, since the water temperature increased also in Kakolanmäki WWTP along the decreased emissions.

Average emission factors could be calculated for both plants based on the two measurement periods. For Kakolanmäki WWTP, the average emission factor is equal to 0.9% of incoming total N load. For Nenäinniemi WWTP, the average emission factor is equal to 1.2% of incoming total N load. WWTPs with total nitrogen removal average to an emission factor of 0.9% of incoming total N (Gruber et al., 2021b). The average emission factor of Kakolanmäki WWTP is equal to this literature value. WWTPs with only nitrification average to an emission factor of 1.8% of incoming total N (Gruber et al., 2021b). The average emission factor of Nenäinniemi WWTP, equal to 1.2%, is lower than the average of nitrification-only plants, which is expected because Nenäinniemi WWTP had denitrification occurring during the summer measurements.

In Kakolanmäki WWTP, the annual carbon footprint of 2021 was estimated based on emission factor equal to 1.2% of N-load, which has similar magnitude to the average emission factor equal to 0.9% (Leino, 2022). In Nenäinniemi WWTP, the annual carbon footprint of 2020 was estimated based on IPCC general emission factor equal to 1.6% of N-load (AFRY, 2022). The average emission factor of Nenäinniemi WWTP during the measurement campaigns was 25% smaller than the default IPCC emission factor. However, the average emission factors are only based on data collected during spring and summer, and do not therefore present annual average. To calculate the annual average emission factor, off-gas N_2O measurements should be conducted during all seasons, preferably continuously for one year, and several compartments should be monitored simultaneously.

Emission factor presents the share of nitrous oxide emissions from the incoming nitrogen load. Therefore, emission factor does not consider the treatment efficiency of the process. During the spring measurement campaigns, the average emission factors were 1.3% of the incoming nitrogen load for Nenäinniemi WWTP and 1.7% of the incoming nitrogen load for Kakolanmäki WWTP. However, the average shares of nitrous oxide nitrogen from the treated total nitrogen were 28.0% for Nenäinniemi WWTP and 1.9% for Kakolanmäki WWTP. Therefore, Kakolanmäki WWTP emitted considerably less N_2O per treated ton of nitrogen compared to Nenäinniemi WWTP despite having slightly higher N_2O emissions per incoming nitrogen load. This raises the question whether the commonly applied emission factor metric that compares N_2O emission to incoming nitrogen load is the best metric to describe the nitrous oxide emissions or should the treatment efficiency be considered when emissions are compared.

5.4 Uncertainties and sources of error

The calculated N_2O-N loads and emission factors include uncertainty due to spatial and temporal limitations on the off-gas N_2O data, the error related to the application of silica filter in Nenäinniemi WWTP, and the error related to the conversion of Nenäinniemi WWTP aeration data to standard units. First source of uncertainty in the N_2O-N load and emission factor estimates is the spatial limitations in data collection. In this thesis, only aerated compartments of the activated sludge process were measured. No emissions stripping from anoxic compartments were accounted because the aeration volumes of these compartments are zero, and the N_2O-N loads were calculated as the product of aeration

volumes and the N_2O concentrations. Neither was other process parts, such as secondary clarifiers studied. Typically, aerated compartments of activated sludge process release around 80% of the N_2O emissions (Gruber et al., 2021b). However, the contribution of secondary clarifiers to the total N_2O can be up to 33% (Mikola et al., 2014). Anoxic compartments of the activated sludge process can contribute to the total emissions, but due to low gas stripping in anoxic compartments, majority of the gases remain dissolved until reaching the aerated compartments with larger air-liquid interface that allows larger gas stripping (Law et al., 2012).

Only one of the aeration lines was studied per plant and all the unmeasured lines were assumed to have equal off-gas N_2O concentrations to the measured one. Assuming equal emissions for lines with common feed source is considered reasonable in *Guideline for the evaluation of nitrous oxide monitoring at WWTPs* by Gruber and Joss (2021a). However, unequal distribution of the feed generally always occurs in WWTPs, which could create differences between the N_2O emissions of aeration lines. To accurately estimate the emissions of each line, measurements should be conducted at all the lines.

Furthermore, measurements should be conducted at several spots along an aeration line simultaneously to accurately estimate the spatial distribution of the N_2O emissions. In this thesis, only one compartment was measured at a time, and the spatial distribution of the emissions was estimated based on two compartments measured consecutively or based on measurements from a single compartment. Thus, some of the observed differences in emissions across compartments might be due to changes in emission levels in time instead of actual differences between compartments. In Kakolanmäki WWTP, no larger than 13% differences were observed in the process conditions, such as load, inflow, pH, alkalinity, or water temperature, within the measurement periods. This suggests that major temporal changes in N_2O concentration are unexpected and the differences between compartments are likely spatial differences. During the Nenäinniemi WWTP spring measurement period, the alkalinity was on average 42% higher, and the BOD load was on average 55% higher during the measurements from compartment 8 compared to the measurements from compartment 1, which might affect the N_2O formation. During Nenäinniemi summer measurements, the incoming COD load was 108% higher during the measurements from compartment 8 compared to the measurements at compartment 4, which might affect the N_2O formation, because higher COD to N ratio typically improves denitrification.

The off-gas concentrations of the unmeasured compartments may significantly differ from the measured ones. Linear regression was applied to estimate the N_2O concentrations of unmeasured compartments in measurement periods in which data from two compartments was collected. However, more than two compartments should be measured in unison to study the spatial distribution of the emissions and the validity of the linearity assumption.

Some of the difference in Kakolanmäki WWTP spring and summer emission factors is likely due to different scopes of data collection. During spring measurements only compartment 6 from line 2 was measured and all the unmeasured compartments were assumed to have equal concentrations to the measured ones. During summer, measurements were conducted at compartments 4 and 6 from line 2, and unmeasured compartments were linearly estimated from the data. During Kakolanmäki WWTP summer measurement campaign, the average N_2O concentration of compartment 4 was 70% lower than the average concentration of compartment 6. Therefore, the spring emission factor of Kakolanmäki WWTP might be an overestimate because it was estimated by assuming all compartments to have the N_2O emissions of compartment 6. However, not all the difference between Kakolanmäki WWTP spring and summer emissions is due to different measurement

scopes: the average compartment 6 off-gas N_2O concentration was 900% larger in spring measurement campaign compared to the summer campaign.

The measurement campaigns conducted in this thesis were short: 15-day and 11-day campaigns were conducted at both plants, which adds to 26 days in total per plant. Due to shortness of data, no annual average emission factors can be calculated based on the results of this thesis. It should be highlighted that the average emission factors calculated do not represent annual averages because they are based on data collected only during spring and summer. In Viikinmäki WWTP, the emissions have generally been lowest during late spring and summer. If this would hold for Kakolanmäki WWTP and Nenäinniemi WWTP, the annual averages are expected to be larger than the calculated averages.

Alongside limitations in the spatial and temporal scopes of the data, factors related to measurement practices create some uncertainty to the results. In Nenäinniemi WWTP, a silica filter was used in the beginning of the spring measurement period, which was observed to affect the results. A constant correction factor was applied to the data collected with the filter despite the error not being constant in time. The subsequent data points without filter and with filter were observed to have differences with magnitudes of 1.6, 2 and 1.4, and 2 was selected as the correction factor. If the smallest correction factor equal to 1.4 would be used, the average emission factor of Nenäinniemi WWTP spring campaigns would decrease to 1.2% of N-load, which is 8% smaller than the estimate given in this thesis.

Another source of error to the emission factor results of Nenäinniemi WWTP arises from the aeration data. The aeration data was collected in non-standardized unit (m^3/h) and required conversion to standard unit (Nm^3/h). The conversion was done by assuming ideal gas and constant temperature and pressure. No changes in relative humidity were considered. During Nenäinniemi WWTP spring measurement campaign, the average emission factor calculated with non-standardized aeration volumes (m^3/h) was 8% smaller compared to the emission factor calculated with the converted standard volumes (Nm^3/h).

6 Conclusions

This thesis studied the nitrous oxide emissions of two Finnish municipal wastewater treatment plants, Kakolanmäki WWTP in Turku and Nenäinniemi WWTP in Jyväskylä. Two measurement campaigns equal to 15 days and 11 days were conducted at both plants. The first campaigns were conducted during March and April and the second campaigns were conducted during May and June. At Nenäinniemi WWTP, measurements were conducted during both nitrifying and total nitrogen removal seasons. Nitrous oxide concentrations were measured from the gas stripping from the aerated compartments of the activated sludge processes. One to two locations were measured per campaign. The measurement setup consisted of an off-gas hood and a Gasmet GT5000 Terra gas analyzer.

Based on the measured off-gas nitrous oxide concentrations combined with the aeration volumes of the activated sludge processes and the total nitrogen loads, nitrous oxide emission factors were calculated for each measurement period. Additionally, the spatial and temporal dynamics of the off-gas nitrous oxide concentrations, and the correlation between the off-gas nitrous oxide and dissolved nitrite were studied. Furthermore, N_2O mitigation measures were suggested for Kakolanmäki WWTP and Nenäinniemi WWTP based on the comparison of the N_2O emission dynamics to the dynamics of process parameters.

The emission factors for Kakolanmäki WWTP spring and summer measurement campaigns were 1.7% and 0.09% of total N-load, respectively. The emission factors for Nenäinniemi WWTP spring and summer measurement campaigns were 1.3% and 1.0% of total N-load, respectively. The measurement campaigns conducted in this thesis were relatively short, in total 26 days per plant. Therefore, no firm conclusions on the annual average N_2O emissions can be made.

Spatial and temporal variance in the nitrous oxide emissions of both Kakolanmäki WWTP and Nenäinniemi WWTP was observed. The emission factors were 1789% and 30% higher during the spring measurement campaigns compared to the summer measurement campaigns at Kakolanmäki WWTP and Nenäinniemi WWTP, respectively. The temperature of the wastewater differed significantly between the two measurement periods at both plants, which could partly explain the differences in emissions. Additionally, Nenäinniemi WWTP was run with denitrification-nitrification configuration during the summer measurements, which increased the total nitrogen removal of the plant from 1% during the spring measurements to 59% during the summer measurements.

The off-gas nitrous oxide concentration exhibited strong temporal variation also within the measurement campaigns, and clear diurnal pattern could be observed in all the measured aeration compartments except in one. The lowest concentrations generally occurred 8–10AM and the highest concentrations 8–11PM. The hourly average off-gas N_2O concentrations during a single measurement period varied from 6% to 432% of the average concentration of the measurement period. This result highlights the need for continuous measurement campaigns to capture the temporal variance of the emissions.

Alongside temporal variation, the off-gas nitrous oxide concentrations differed up to 236% between the compartments of an aeration line. This result highlights the need for several measurement locations to capture the spatial variance of the emissions, if the measurements are conducted from the gas stripping from the aeration basins. The exhaust gas line for indoor plants would account gases stripping from all process parts and would therefore give more comprehensive results.

Moderate positive correlation (Pearson correlation = 0.57) between the dissolved nitrite and off-gas nitrous oxide was found from all the nitrite and nitrous oxide data from

Kakolanmäki WWTP and Nenäinniemi WWTP.

At Kakolanmäki WWTP, several possible N_2O mitigation measures could be pointed out: increasing the COD to N ratio, maintaining the compartment 6 DO concentration close to 1.8 mg/l, increasing the SRT during nitrite accumulation, and increasing the alkalinity. Research should be conducted to test the effectiveness of these strategies.

At Nenäinniemi WWTP, full nitrogen removal could be and effective N_2O mitigation measure, since the emission factor was 23% lower during the measurement campaign conducted during the total nitrogen removal season. However, the effect of denitrification on N_2O emissions should be studied further to rule out the effect of water temperature increase, since the water temperature increased also in Kakolanmäki WWTP along the decreased emissions.

The results of this thesis provide initial understanding on the dynamics and magnitude of the N_2O emissions of Kakolanmäki WWTP and Nenäinniemi WWTP. However, to provide estimates on the annual average emission factors and to study the effects of mitigation measures, longer campaigns should be conducted with measurement conducted at several aeration compartments simultaneously. Or in the case of Kakolanmäki WWTP, which is located inside, plant exhaust gas line N_2O concentrations could be measured.

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